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PACE Report No. 87-3

EVALUATION OF SMALL SCALE RETARDATION TESTS FOR BTX IN GROUNDWATER

"Working for a Better Environment"

EVALUATION OF SMALL SCALE RETARDATION TESTS FOR BTX IN GROUNDWATER

PACE Report No. 87-3

Prepared for

Petroleum Association for Conservation
of the Canadian Environment (PACE)
1202 - 275 Slater Street
Ottawa, Ontario K1P 5H9

American Petroleum Insitute (API)

Environment Canada

by

R.W. Gillham, S.F. O'Hannesin,
C.J. Ptacek, J.F. Barker
Institute for Groundwater Research
University of Waterloo

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NOTICE

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EXECUTIVE SUMMARY

Preamble

This report provides the results from one part of a research study concerning Benzene, Toluene and Xylene (B, T, X) contamination of groundwater.

The specific objectives of the research program are: 1) to critically evaluate small-scale methods for measuring the retardation caused by sorption of the aromatic hydrocarbons (B, T, X) as they move in groundwater, 2) to determine the effects of both retardation by sorption and biodegradation on the migration of BTX in groundwaters, and 3) to assess the potential for biochemical remediation or clean-up of groundwaters contaminated by BTX.

This report addresses the first objective; evaluation of small-scale laboratory techniques to measure retardation factors. Specific study objectives were:

1. to examine the range of retardation factors that could be expected for the soluble constituents of petroleum products in typical aquifer materials
2. to critically evaluate the various small-scale laboratory methods that can be used to estimate the sorptive retardation character of aquifer materials.

Retardation factors are used to calculate the rate at which a contaminant moves relative to the velocity of the groundwater and are therefore useful in evaluating the potential environmental impact of the dissolved constituents at a spill site. The results of this study indicate a range of retardation factors that could generally be expected for the soluble constituents of gasoline, and suggest the most practical means of measuring retardation factors for these materials.

The Phase I Report (PACE Report No. 85-3) and Phase II Report (PACE Report No. 86-1) describe the design, implementation and analysis of a field experiment where BTX

dissolved in groundwater was injected below the water table of a shallow sand aquifer. The migration of BTX was monitored as it moved under natural hydraulic gradients through a dense network of monitoring wells. The BTX migrated at velocities lower than that of the groundwater due to sorption by solid organic material in the aquifer, and the amount of BTX decreased over time due to biodegradation. In the field experiment the rate of migration was shown to be reasonably consistent with predictions based on measurements of the retardation factors using small-scale laboratory procedures and a small-scale in situ column procedure.

Small-Scale Retardation Tests

Retardation factors are generally calculated on the basis of the extent to which a contaminant is chemically partitioned between the solution and solid phases of a porous medium. This chemical partitioning is represented by a parameter referred to as the distribution coefficient (K_d). Various methods for predicting the distribution coefficient in groundwater were examined. Each method involved measurement of the partitioning coefficient (K_d) of dissolved organic compounds between the solution phase and the solid phase of various aquifer materials. The procedures examined included 1) correlations based on the solid organic carbon content of the aquifer material (f_{oc}) 2) laboratory batch procedures 3) laboratory column procedures and 4) a small-scale in situ column procedure. Aquifer materials were collected from eight locations in southern Ontario. The materials ranged in texture from medium sand to silt and had values of organic carbon content (f_{oc}) ranging from 0.00017 to 0.00108 g/g. The organic compounds used in the tests were benzene, toluene, m-xylene, o-xylene, p-xylene and naphthalene.

All methods showed similar trends in the K_d values, and were consistent with the theory of sorption of slightly soluble (hydrophobic) organic compounds in soil materials. In particular, all soils and all methods showed increasing uptake by the solid phase with

increasing hydrophobicity of the compounds. Furthermore, though several exceptions were noted, sorption tended to increase with increasing f_{oc}.

K_d values for the most weakly sorbed compound, benzene, ranged from 0.03 to 0.09 mL/g, while values for the most strongly sorbed, naphthalene, ranged from 0.15 to 2.0 mL/g. Thus, depending upon the properties of the particular compound and the particular soil, K_d values can be expected to range over more than two orders of magnitude. In addition, the range is important because at the lower end, the compound would be virtually unretarded, while at the high end of the range the compound would be highly retarded. Accurate evaluation of K_d values would therefore be important in the management of groundwater zones contaminated by petroleum products.

Though there were exceptions, all methods gave reasonably similar K_d values. Based largely on ease and low cost, the method involving correlations with the organic carbon content of the soil is the most suitable method for obtaining a first approximation of the K_d values. It requires accurate measurements of f_{oc} however, and these values generally have a high degree of uncertainty in aquifer materials that contain small amounts of organic carbon. Because of the empirical nature of the equations used in this method a further degree of uncertainty is unavoidable when considering a particular organic in a particular soil. If more accurate estimations of K_d are required, such as in the design of remediation schemes, where the cost of a misjudgement is high, it is recommended that the initial K_d estimates, based on the correlation equation method, be supplemented with batch or column tests.

S O M M A I R E

Préambule

Le présent rapport donne les résultats d'une partie d'un programme de recherche sur la contamination des eaux souterraines par le benzène, le toluène et le xylène (B, T, X).

Les objectifs précis du programme sont les suivants: 1) évaluer de façon critique les méthodes de mesure à petite échelle du ralentissement des hydrocarbures aromatiques (B, T, X) sous l'effet de la sorption lorsqu'ils se déplacent dans les eaux souterraines, 2) déterminer les effets du ralentissement par sorption et biodégradation sur la migration des BTX dans les eaux souterraines, et 3) évaluer les possibilités de traitement correctif ou d'épuration biochimiques des eaux souterraines contaminées par les BTX.

Le présent rapport traite du premier objectif: évaluer les techniques de laboratoire permettant de mesurer à petite échelle les facteurs de ralentissement, et plus précisément:

1. examiner la gamme des facteurs de ralentissement auxquels on pourrait s'attendre pour les constituants solubles des produits du pétrole dans des matières aquifères caractéristiques;
2. évaluer de façon critique les diverses méthodes de laboratoire qui peuvent servir à estimer à petite échelle le ralentissement par sorption dû aux matières aquifères.

Les facteurs de ralentissement servent à calculer la vitesse à laquelle un contaminant se déplace par rapport à la vitesse des eaux souterraines et ils sont donc utiles pour évaluer les incidences environnementales potentielles des constituants dissous à un endroit de déversement. Les résultats de la présente étude donnent une gamme de facteurs de ralentissement que l'on pourrait généralement prévoir pour les constituants solubles de l'essence et ils permettent de proposer les moyens les plus pratiques de mesurer les facteurs de

ralentissement pour ces matières.

Les rapports de la phase I (PACE Report No. 85-3) et de la phase II (PACE Report No. 86-1) décrivent la conception, la mise en oeuvre et l'analyse d'une expérience sur le terrain au cours de laquelle des BTX dissous dans des eaux souterraines ont été injectés sous la nappe phréatique d'une couche de sable aquifère à faible profondeur. Au moyen d'un réseau dense de puits de contrôle, on a surveillé la migration des BTX qui se sont déplacés sous l'effet de gradients hydrauliques naturels. Les BTX ont migré à des vitesses inférieures à celle des eaux souterraines à la suite de la sorption par des matières organiques solides dans la couche aquifère, et la quantité des BTX a diminué avec le temps par suite de la biodégradation. Au cours de l'expérience sur le terrain, on a montré que la vitesse de migration correspondait d'assez près aux prévisions établies à partir de mesures des facteurs de ralentissement effectuées à l'aide de procédures de laboratoire à petite échelle et d'une procédure sur colonne in situ à petite échelle.

Tests de ralentissement à petite échelle

En général, pour calculer les facteurs de ralentissement, on étudie dans quelle mesure un contaminant est séparé chimiquement entre la phase de solution et la phase solide d'un milieu poreux. Cette séparation chimique est représentée par un paramètre appelé coefficient de distribution (K_d). On a examiné diverses méthodes de prévision du coefficient de distribution dans les eaux souterraines. Chaque méthode comprend la mesure du coefficient de séparation (K_d) de composés organiques dissous entre la phase de solution et la phase solide de diverses matires aquifères. Les procédures examinées comprennent: 1) les corrélations sur la base de la teneur en carbone organique solide de la matière aquifère (f_{oc}); 2) les procédures de laboratoire en série; 3) les procédures de laboratoire sur colonne; et 4) une procédure sur colonne in situ à petite échelle. Des matières aquifères ont été prélevées à huit endroits du sud de l'Ontario. Leur texture va du sable moyen au limon et leur teneur en carbonne organique (f_{oc}) varie entre 0,00017 et 0,00108 g/g. Les composés organiques utilisés pour les tests sont le benzène, le toluène, le

m-xylène, l'o-xylène, le p-xylène, et le naphtalène.

Pour toutes le méthodes, on a observé des tendances similaires dans les valeurs K_d, et les résultats sont conformes à la théorie de la sorption de composés organiques légèrement solubles (hydrophobes) dans les matières du sol. En particulier, tous les sols et toutes les méthodes ont indiqué une absorption croissante par la phase solide avec l'augmentation de l'hydrophobie des composants. En outre, malgré quelques exceptions, la sorption tendait à augmenter en même temps que f_{oc}.

Les valeurs K_d pour le composant le plus faiblement adsorbé, le benzène, variaient entre 0,03 et 0,09 mL/g tandis que les valeurs pour le composant le plus fortement adsorbé, le naphtalène, allaient de 0,15 à 2,0 mL/g. Par conséquent, selon les propriétés d'un composé ou d'un sol donné, on peut s'attendre à ce que les valeurs K_d s'échelonnent sur plus de deux ordres de grandeur. En outre, la gamme est importante car au bas de la gamme, le composé ne serait pratiquement pas ralenti tandis qu'en haut de la gamme, le composé serait fortement ralenti. Il serait donc important d'évaluer avec précision les valeurs K_d pour traiter les zones d'eaux souterraines contaminées par des produits du pétrole.

Malgré quelques exceptions, toutes les méthodes ont donné des valeurs K_d assez similaires. La méthode comprenant des corrélations avec la teneur du sol en carbone organique est la méthode la plus appropriée pour l'obtention d'une première approximation des valeurs K_d, surtout à cause de sa facilité d'emploi et de son faible coût. Cependant, il faut mesurer les valeurs f_{oc} avec précision et ces valeurs ont généralement un degré d'incertitude élevé dans les matières aquifères qui contiennent de petites quantités de carbone organique. A cause de la nature empirique des équations utilisées dans cette méthode, un autre degré d'incertitude est inévitable lorsqu'on considère un composé organique donné dans un sol donné. Si des estimations plus précises de K_d sont nécessaires, comme pour la conception de plans de mesures correctives, où une erreur de jugement coûte cher, il est recommandé d'effectuer des tests sur colonne ou en série dont les résultats viendront compléter les estimations initiales de K_d obtenues avec la méthode de l'équation de corrélation.

CONTENTS

INTRODUCTION 1
Background 1
K_d Concepts 2
Objectives and Scope 4

METHODS 6
Materials 6
Correlation Procedures 12
Batch Procedures 14
Laboratory Column Procedures 15
In Situ Column Experiments 19
Analytical Methods 21

RESULTS AND DISCUSSION 23
Static Tests 23
Dynamic Tests 35
Comparison of Methods 50

CONCLUSIONS 52

Glossary of Contaminant Hydrogeology Terms 54

References 56

TABLES

1. Aqueous solubility and octanol-water partitioning coefficients of the organic compounds used in the study 7

2. Characteristics of the geologic materials 11

3. Results of K_d determinations using correlation equations based on f_{oc} and as determined from the batch tests. 24

4. Comparison of distribution coefficients for Borden sand. 41

5. Comparison of distribution coefficient for Rodney sand. 48

6. Summary of advantages and disadvantages of the small-scale K_d tests used in this study 51

FIGURES

1. Map showing the locations at which the geologic samples were collected 8

2. Schematic of column used in the laboratory experiments. 17

3. Schematic of the laboratory column apparatus. 18

4. Schematic of the field column device 20

5. Sorption isotherms 27

6. Laboratory column results for Borden sand, v = 22 cm/day. 36

7. Laboratory column results for Borden sand, v = 150 cm/day. 37

8. Field column results for Borden sand, v = 340 cm/day. 39

9. Field column results for Borden sand, v = 190 cm/day. 40

10. Breakthrough curve for the non-reactive tracer (tritium) in Rodney sand (v = 224 cm/day) 43

11. Laboratory column result from Rodney sand, v = 37 cm/day. 44

12. Laboratory column result for Rodney sand, v = 75 cm/day. 45

13. Laboratory column result for Rodney sand, v = 224 cm/day. 46

14. Result of field column test for Rodney sand, v = 465 cm/day. 47

1

INTRODUCTION

1.1 Background

The soluble constituents of petroleum products have a significant potential to cause contamination of the groundwater environment. This argument is based on the large number of potential sources of contamination, the fact that many of the potential sources occur as storage tanks buried below ground surface, and the very low drinking water limits for these compounds. For example, the World Health Organization has established a drinking water limit for benzene of 10 $\mu g/L$.

Though major efforts by the petroleum industry are being directed at reducing the number and severity of leaks and spills, it is not realistic to expect that accidental releases of petroleum products to the subsurface environment will be eliminated. It is therefore important that the technology be available for dealing with these releases when they do occur. An important aspect of this technology concerns the ability to predict the future distribution of contaminated zones of groundwater associated with a particular spill. This predictive capability may be applied to natural conditions of groundwater flow to assess the need for remedial action and may be particularly useful in the design and evaluation of remedial programmes.

This particular report addresses one aspect of the predictive problem: geochemical retardation of selected soluble constituents of petroleum products. There are two principal objectives: to examine the range of retardation factors that could be expected for several soluble constituents of petroleum products over a range of aquifer materials, and to evaluate various methods for determining retardation factors.

1.2 K_d Concepts

As discussed in greater detail in Cherry et al. (1984) and Patrick et al. (1986), the principal processes affecting the migration of dissolved organic contaminants in groundwater include the bulk motion of the fluid phase (advection), mixing caused by velocity variations within the geologic material (dispersion), geochemical processes such as sorption, and biochemical processes including biodegradation and biotransformation. These can be represented in the commonly accepted advection-dispersion equation, which, for one-dimensional flow and transport can be written

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial z} - Q \qquad [1]$$

where C is the concentration of the contaminant in the solution phase (ML^{-3}),[1] t is time (T), D is the dispersion coefficient (L^2T^{-1}), x is the cartesian space coordinate in the direction of flow (L), V is the average groundwater velocity (LT^{-1}) and Q is a general sink term that represents the rate of loss of contaminant from the solution phase by all processes (geochemical and biochemical) ($ML^{-3}T$). The first term on the right hand side represents the effects of dispersion while the second term represents the effect of the bulk motion of the fluid phase. Solutions to eq. 1 give the solute concentration at any point within the region of interest, at any future time; however, before a solution can be derived, the character of the sink term, Q, must be specified. For the purpose of this investigation, only sorption processes will be considered, in which case, following Lapidus and Amundson (1952) and Bear (1972), eq. 1 can be written

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - V \frac{\partial c}{\partial z} - \rho/\eta \, K_d \frac{\partial C}{\partial t} \qquad [2]$$

---

[1] In this report the dimensions of the various parameters are expressed in terms of the three basic physical quantities (mass, length and time), using the convention M, L and T.

where ρ is the bulk density of the porous medium (ML^{-3}), n is porosity (L^3L^{-3}) and K_d is the distribution coefficient (L^3M^{-1}). The distribution coefficient represents the partitioning of the solute between the solution and solid phases, and is defined as the concentration of the solute in the solid phase divided by the concentration in the solution phase. As included in eq. 2, the reaction term is only appropriate for reactions that are instantaneous and reversible and where the concentration in the solid phase is a linear function of the concentration in the solution phase. These are the conditions of a linear sorption isotherm, with K_d being the slope of the isotherm. The assumptions inherent in eq. 2 are discussed further in Cherry et al. (1984).

The practical significance of retardation processes becomes more evident if the dispersion term of eq. 2 is neglected. In this case, eq. 2 becomes

$$V_s = V/R \qquad [3]$$

This shows the velocity of the solute (V_s) to be equal to the groundwater velocity (V) divided by the retardation factor (R), defined by

$$R = 1 + (\rho/\eta)\, K_d \qquad [4]$$

For a species that does not react with the solid phase of the porous medium, K_d=0 giving a retardation factor of 1.0 and thus a velocity equal to that of the groundwater. On the other hand, the velocity of a reactive species is less than that of the groundwater by a factor of 1/R. The ratio ρ/n for granular unconsolidated geologic materials generally varies over the relatively small range of about 4 to 6. Assuming an average value of 5, the contaminant velocity will generally be about $1/(1 + 5\ K_d)$ times that of the groundwater. Clearly, the contaminant velocity is strongly dependent upon the magnitude of K_d.

In a field-scale tracer test conducted in a medium to fine grained sand aquifer, Patrick et al. (1986) reported average retardation values for benzene (1.1), toluene (1.2), o-xylene (1.4), p-xylene (1.4) and m-xylene (1.6). Consistent with recent theory, the retardation factors increased with decreasing solubility of the compounds and increasing octanol-water par-

titioning coefficient (K_{ow}). Furthermore, the values were similar to (though somewhat less than) values calculated on the basis of the solid orga. c carbon content of the aquifer material (f_{oc}) and values measured using small-scale laboratory methods.

It should first be noted that the retardation values are relatively small, suggesting that in this particular aquifer, benzene and m-xylene, the extreme cases, would migrate at velocities of about 90% and 40% respectively of the groundwater velocity. As a result, considering the uncertainties of boundary conditions and the other parameters of predictive models, little credit can be taken for retardation as a mechanism that would significantly increase the time of arrival of the contaminants at an environmentally sensitive location in the groundwater flow system. On the other hand, if one chooses to remediate an aquifer by pumping, even a small retardation factor (1.5 for example) could increase the time and operating cost of the rehabilitation project by about 50% over predictions based on non-reactive contaminants. Furthermore, as demonstrated by Patrick et al. (1986) even small retardation factors can be of major importance in in situ remediation. Under natural conditions, aromatic hydrocarbons tend to biodegrade readily under oxidizing conditions but only slowly or not at all under anoxic conditions. Consequently, when the oxygen in the groundwater is depleted, the biodegradation process essentially stops. However, if the contaminants are retarded, oxygen would be continually replenished by fresh groundwater that overtakes the plume. Similar processes would occur in enhanced remediation schemes where oxidants such as peroxide or nitrate are added to the groundwater behind the plume.

1.3 Objectives and Scope

As indicated in the previous discussion, retardation factors have considerable application in the management of groundwater zones contaminated by petroleum products. At the present time there is an insufficient technological basis for evaluating the significance of retardation with respect to a specific site. The specific objectives of this study are to pro-

vide an improved appreciation of the range of retardation values that can be expected in aquifer materials and to provide further knowledge concerning the most appropriate methods for evaluating retardation factors.

Distribution coefficients (K_d) were measured for benzene, toluene, p-xylene and naphthalene (BTXN) in eight aquifer materials. For all materials, K_d values were determined using published correlations between the f_{oc} of the aquifer material and the aqueous solubility and K_{ow} of the compounds. Values were also determined for all compounds and soils using equilibrium batch procedures. In addition, K_d values were determined for two soil materials using laboratory column procedures and a recently developed in situ column procedure.

2

METHODS

2.1 Materials

The organic compounds used in the study included benzene, toluene, o-, m-, p-xylene and naphthalene. These were obtained as analytical grade compounds, while benzene, toluene, p-xylene and naphthalene were also obtained as carbon-14 labelled compounds. The compounds, along with their aqueous solubilities and octanol-water partitioning coefficients (K_{ow}) are given in Table 1.

The aquifer materials were collected from sites at which detailed hydrogeologic investigations had been conducted previously or were in progress. The samples were generally collected from below the water table using core-sampling equipment, and were air dried for storage prior to conducting the tests. The sampling locations are indicated in Figure 1 and selected sample characteristics are included in Table 2.

Brief descriptions of the samples are given below, along with references that give more detailed descriptions of the local hydrogeologic conditions.

North Bay (Barker et al., 1986) This sample was collected from the sand aquifer in the vicinity of the North Bay landfill site. The sample was taken from an uncontaminated area of the aquifer over a depth interval of about 3 to 10 m. As discussed in the reference, the sand varies in texture from coarse to very fine, and does not contain carbonate minerals. The particular sample collected for use in this study was classified as medium sand.

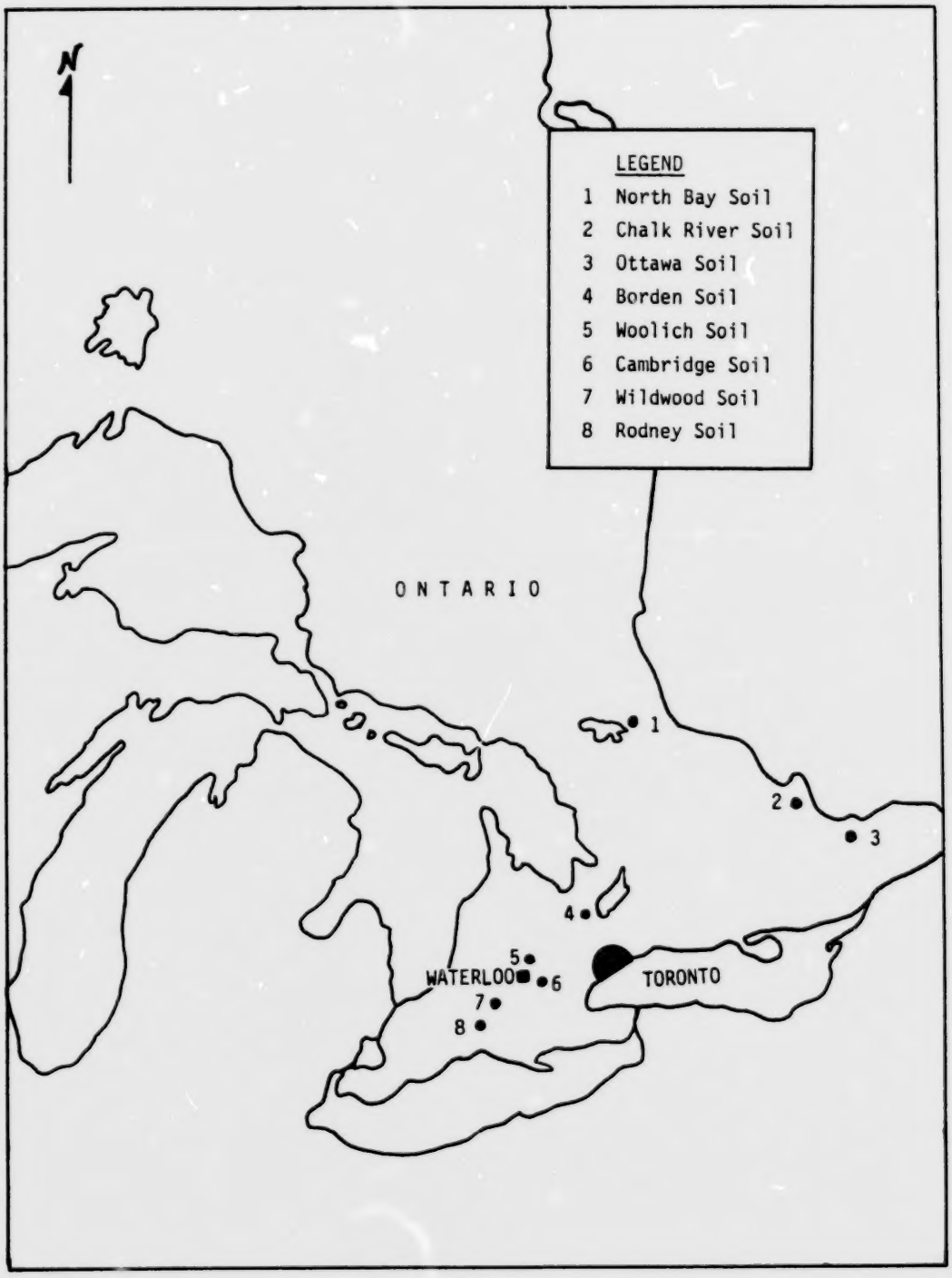
Table 1: Aqueous solubility and octanol-water partitioning coefficients of the organic compounds used in the study

	CHEMICAL FORMULA	AQUEOUS SOLUBILITY S (PPM) *	OCTANOL-WATER PARTITIONING COEFFICIENT (K_{ow}) **
Benzene	C_6H_6	1740	140
Toluene	C_7H_8	554	380
O-Xylene	$C_6H_4(CH_3)_2$	167	880
M-Xylene	$C_6H_4(CH_3)_2$	134	1580
P-Xylene	C_8H_{10}	157	1410
Naphthalene	$C_{10}H_8$	32	2594

* Values from Kebe and Brookman, 1984

** Average of selected values from Hansch and Leo, 1979

Figure 1: Map showing the locations at which the geologic samples were collected



Chalk River (Gillham et al., 1980) The Chalk River sample was collected from the Perch Lake Basin of Atomic Energy Canada Limited. It was collected using a shovel at a depth just below the water table, about 1 m below ground surface. Though carbonate minerals are present in the sand, they generally represent less than 1% of the dry weight.

Borden (Cherry, 1983; Patrick et al., 1986) The Borden sample was collected from the site of the natural gradient tracer test described in Patrick et al. (1986). The sample was collected over a short vertical interval just below the water table, about 1 m below ground surface.

Woolwich (Cherry, 1983) The Woolwich sample was taken from an uncontaminated region of the sand aquifer at the Woolwich landfill site. The sample consisted of sub-samples taken from core material collected over a depth interval of about 5 m to 15 m. The sand has a high carbonate mineral content and the particular sample used in this study was classified as a fine to medium sand.

Wildwood (Starr, 1985) Unlike the other materials, the Wildwood sample, because of its fine texture (silt), is not an aquifer material. It was collected using a shovel from below the water table, in a groundwater discharge region at the base of a road cut. Though the sample has a high carbonate content and is classified as a silt, we have no further background information concerning its geochemical characteristics or the local hydrogeolgic conditions.

Cambridge (Presant and Wicklund, 1971) This sample was collected at the Cambridge Research Station of the Ontario Ministry of Agriculture and Food. The principal surficial geologic material at the site is sand, but of highly variable texture. The particular sample used in this study was collected over a 3 m vertical interval below the water table. It has a high carbonate mineral content and the composite sample was classified as a medium sand.

Ottawa (Jackson et al., 1985) Core samples were collected at a depth of about 7 m below ground surface at the Gloucester landfill site. This particular site was chosen because the sand had previously been reported to have a high f_{oc} value.

Rodney (Trudell et al., 1986) The Rodney site was located in an agricultural area. Previous studies had indicated relatively high f_{oc} values in the vicinity of the water table, which was located at a depth of about 1 m below ground surface. The geologic material was a fine-grained sand, and samples were collected over the depth interval of about 1 to 3 m below ground surface.

The only sample characterization that was undertaken as part of this study was measurement of f_{oc} (Table 2). To determine the f_{oc} values, the total carbon was quantified in the soil sample after the removal of inorganic carbon with an acid pretreatment.

In the pretreatment procedure a finely ground, dried soil was weighed into a beaker. It was then slurried in organic-free water and 50% HCl was added dropwise, until effervescence ceased. With a pH of approximately 1.0, the sample sat overnight and was filtered through 0.45 μm filter paper. In order to remove the acid, the sample was washed three times with organic-free water and the water was evaporated off. The sample was then isolated and weighed. An aliquot of the prepared, carbonate-free dried soil sample was weighed into a porcelain combustion boat, then placed in a Lindberg Tube Furnace at 800°C with oxygen flowing through it. The carbon that was present in the sample was completely oxidized to carbon dioxide which was detected by a non-dispersive infrared detector (Beckman, Model 864). A Spectra-Physics integrator processed the signal which was matched up to a standard curve. The standard curve was produced by combusting various weights of pure carbon diluted with pumice. Thus, the weight of organic carbon in a measured weight of carbonate-free soil was determined. This weight is reported as a percent or as a fraction of the weight of the original sample and so yields the % organic carbon or the fraction of organic carbon (f_{oc}) in the sample.

Table 2: Characteristics of the geologic materials

	TEXTURE	DEPOSITIONAL ENVIRONMENT	ORGANIC CARBON CONTENT (f_{oc}) (g/g)
North Bay	medium sand	glacio-fluvial	0.00017
Woolwich	fine to medium grained sand	glacio-fluvial	0.00023
Chalk River	fine sand	glacio-fluvial	0.00026
Borden	fine to medium sand	glacio-fluvial	0.00028
Ottawa (Gloucester)	fine to medium sand	fluvio-glacial	0.00060
Cambridge	medium sand	glacio-fluvial	0.00065
Rodney	fine grained sand	glacio-lacus-trine	0.00102
Wildwood	silt	lacustrine	0.00108

Simulated groundwater was used in conducting the laboratory batch and column tests. Water having the same composition was used for all soil materials. Because most of the soil samples contained carbonate materials, it was considered desirable to use water that would prevent the dissolution of these minerals. It was also considered important that the water be free of organic compounds.

To remove organic compounds from the simulated groundwater, deionized water was passed through activated charcoal, irradiated with ultraviolet light for 30 minutes. To prevent carbonate dissolution the water was prepared such that it was in equilibrium with carbonate mineral at the atmospheric partial pressure of CO_2. Calcium carbonate was added to the water at a concentration that would occur in pure water in equilibrium with calcite at atmospheric p CO_2. The solution was then purged with pure CO_2 to rapidly dissolve the carbonate, and then with purified air at atmospheric p CO_2 until the pH was constant. The pH of the simulated groundwater was approximately 8.3.

Stock solutions were prepared by spiking the simulated groundwater with a concentrated methanol solution containing the appropriate organic compounds. In experiments where the analyses were performed by gas chromatography, the methanol solutions contained benzene, toluene and the three isomers of xylene. Where carbon-14 was used as a tracer, different methanol solutions were used for each compound (benzene, toluene, p-xylene and naphthalene). In all cases the volume of the methanol spike was less than 400 μL per litre of simulated groundwater.

2.2 Correlation Procedures

For solutes that have a positive or negative charge, K_d values are dependent on all factors that affect the exchange process, including the exchange properties of the porous medium, the concentration of the species of interest, the exchange characteristics of the competing ions and the ionic strength of the solution phase. Thus the K_d model for pre-

dicting the migration of ionic contaminants has received severe criticisms (Reardon, 1981). However, for non-polar organic compounds, evidence indicates K_d values to be relatively independent of the ion exchange properties of the medium and the ionic strength and major ion chemistry of the solution phase. Rather, for many sediment-water systems, the distribution coefficients for many nonionic organic compounds have been observed to increase in proportion to the solid phase organic matter content of the matrix (Chiou et al., 1979; Schwarzenbach and Westall, 1981; Karickhoff, 1981 and 1984). This has led to the introduction of the organic carbon partitioning coefficient (K_{oc}) which has been found to be relatively constant for a wide range of sediments and soils (Karickhoff, 1981; Chiou et al., 1979). As a result, the distribution coefficient can be related to the organic carbon content by

$$K_d = f_{oc}\,(K_{oc}) \qquad [5]$$

Many methods have been proposed to estimate K_{oc}, as reviewed recently by Karickhoff (1984). The most commonly used methods are based on semi-empirical correlations with the aqueous solubility, S, or the octanol-water partitioning coefficient, K_{ow}. Typically linear regression equations of the following form are used

$$\log K_{oc} = A \log K_{ow} + B \qquad [6]$$

$$\log K_{oc} = -C \log S + D \qquad [7]$$

in which A, B, C, and D are regression -fitted parameters. In general, the more nonpolar a molecule, the lower its water solubility and the larger its K_{oc} and K_{ow} values. Equations 6 and 7 have been observed to successfully predict the sorption of a large number of hydrophobic solutes onto a wide range of materials, particularly for sorbents with high organic carbon contents, and at low concentrations of the sorbate. The predictions have been less successful for compounds having high polarity and for sorbents with low organic carbon contents, especially with a coincident high clay content. A recent review by Min-

gelgrin and Gerstl (1983) outlines many of the limitations of the above regression models.

The regression coefficients of eq. 6 and 7 have been found to vary slightly, depending on the compounds and the sediments used. The coefficients used in this study were those reported by Schwarzenbach and Westall (1981), (A=0.72, B=0.49,) and by Chiou et al. (1979), (C=0.56, D=4.30). These values were used because they appeared to be the most appropriate for materials of low f_{oc}. After determining the K_{oc} values, the distribution coefficients (K_d) were obtained from eq. 5, using the f_{oc} values of Table 2.

2.3 Batch Procedures

Batch sorption isotherms were determined by equilibrating aqueous solutions of the different carbon-14 labelled hydrocarbons with the geologic materials. Approximately 60 g of sediment were weighed into 60-mL glass crimp-top hypovials fitted with open-holed caps and Teflon-lined septums. A 20 mL aliquot of simulated groundwater was added and agitated to eliminate air bubbles. At the onset of a sorption experiment, approximately 20 mL of the solution containing a particular hydrocarbon was quickly added to the vials containing the simulated groundwater and sand. This resulted in a solid .o liquid ratio of 1.5:1. As controls, two hypovials not containing sand were also filled to determine the initial hydrocarbon concentration; one immediately before and the other after the addition of the hydrocarbon solutions to the sediment samples. The vials were immediately capped leaving a minimum headspace to avoid vapour loss. The samples and controls were equilibrated at 10°C ± 0.5°C for 48 hours on an apparatus that inverted the sample vials every 1 min. Following equilibration, the sediments were removed from suspension by centrifigation (2,000 rpm, 828 x gravity for 30 minutes). In all the experiments, the quantities of sediment and water were determined gravimetrically and all tests were performed in triplicate.

To determine the concentration of hydrocarbons remaining in solution after equilibration, a constant volume of supernatant was syringed directly out of the hypovials and placed in scintillation cocktail. The concentration of each sample was determined as the average of two duplicate determinations. The liquid scintillation counting procedures are described below.

For calculation purposes it was assumed that the difference between the initial solution concentration, taken as the mean of the two control concentrations, and the equilibrium supernatant concentration could be attributed entirely to sorption onto the sediment phase. To assess the accuracy of this assumption, samples of the hydrocarbon solutions were analyzed immediately before and after the addition of the solutions to the control and sediment samples. These values were compared with the control concentrations after the equilibration period. Very small losses were observed, indicating that only minor errors were introduced by calculating the solid phase concentrations as described.

The tests were conducted at six initial concentrations in the equilibrating solution, ranging from about 250 to 4000 $\mu g/L$. This gives 6 points on each isotherm.

Batch tests were initially conducted using the non-labelled compounds; however, because of the very low K_d values that were encountered for most soils, the analytical uncertainty resulted in a high degree of scatter in the data and thus a high degree of uncertainty in the measured K_d values. The use of carbon-14 labelled compounds allows for analysis by scintillation counting procedures, resulting in greater analytical precision, particularly at low concentrations.

2.4 Laboratory Column Procedures

Column experiments are generally conducted by establishing a steady flow of water through a column of the porous medium, and at a particular time, the tracer of interest is introduced at the inflow end of the column. A graph of the trace concentration in the

effluent versus time is referred to as a breakthrough curve. Retardation factors can then be determined from the characteristics of the breakthrough curve.

A 10-cm long by 8.5 cm diameter glass column with stainless steel end-plates was packed homogeneously with the air-dried soil materials. The stainless steel end-plates were designed to facilitate one-dimensional flow within the sand column and to obtain uniform and reproducible concentration fronts at the onset of each experiment. A schematic of the column design is shown in Figure 2. A seal was created at each end of the column with an expanded O-ring seated between the glass column and the end-plates. A variable speed, four-channel Ismatic IP-4 peristaltic pump was used to maintain uniform flow rates throughout the experiments. Effluent solution was collected with an automated collection system. A schematic of the apparatus is shown in Figure 3. The surfaces that contacted the tracer solution were made of Teflon, glass or stainless steel, thus avoiding sources or sinks for the solutes being analyzed.

Saturation of the column proceeded by passing CO_2 gas through the column until the air was displaced, followed by slowly wetting the column from the bottom with the equilibrating solution. The saturated column was then flushed with equilibrating solution for several days to allow the pore-water chemistry to stabilize. Pulse-input experiments in which a small volume of tracer was injected over a one minute period were used. These experiments proceeded by simultaneously injecting chloride as the conservative tracer and the organic solutes as non-labeled compounds. The laboratory column experiments were conducted at 23 ± 1 °C. The concentration of each of the organic solutes in the injected solution was approximately 10 mg/kg.

To conduct an experiment, a glass syringe filled with tracer solution was connected to a line leading to a 3-way valve, the valve was opened to the input line, and the solution was injected into the influent end-plate over a one minute period. After the injection was complete, flow of the nontracer solution was resumed.

Figure 2: Schematic of column used in the laboratory experiments.

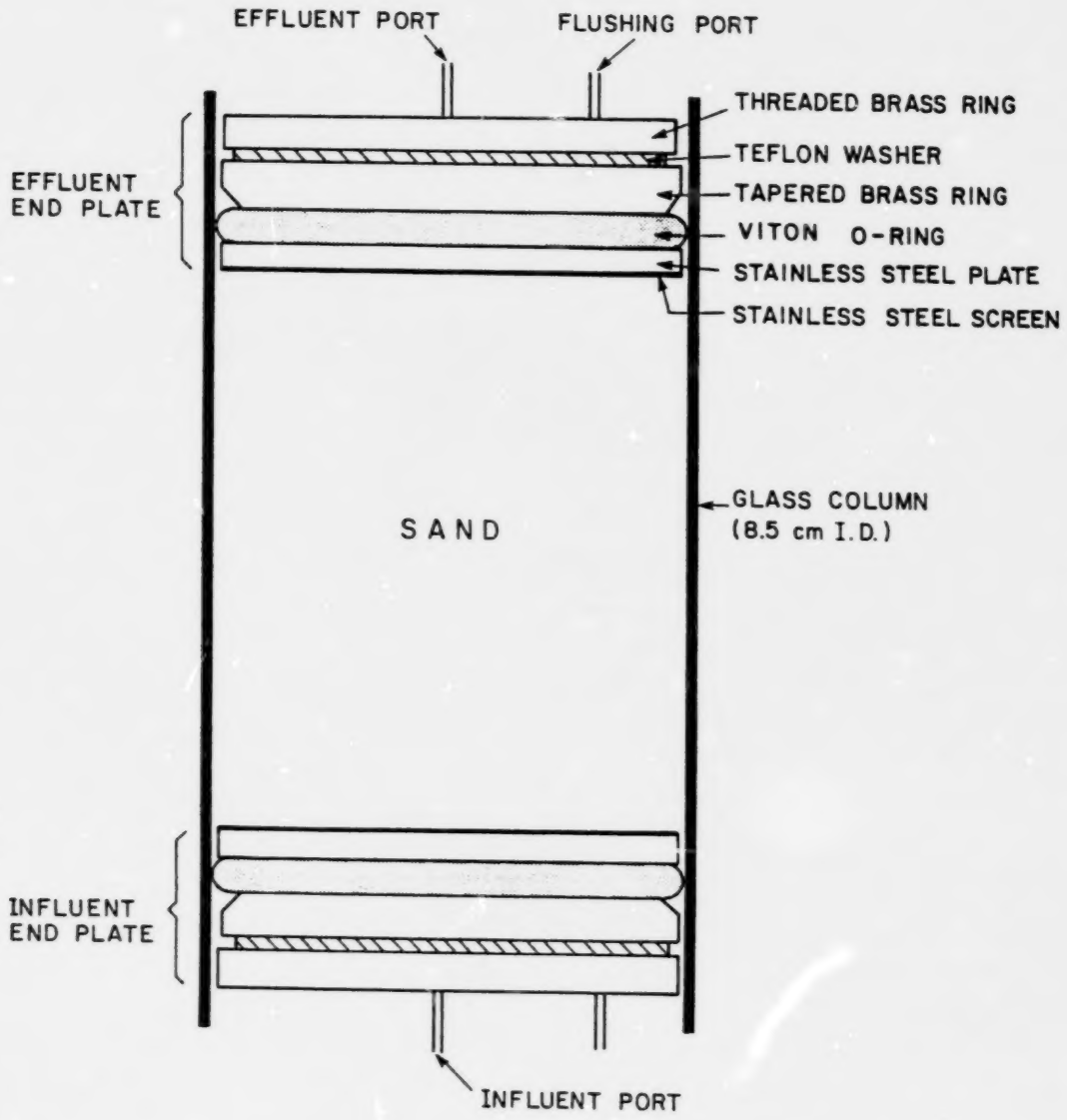
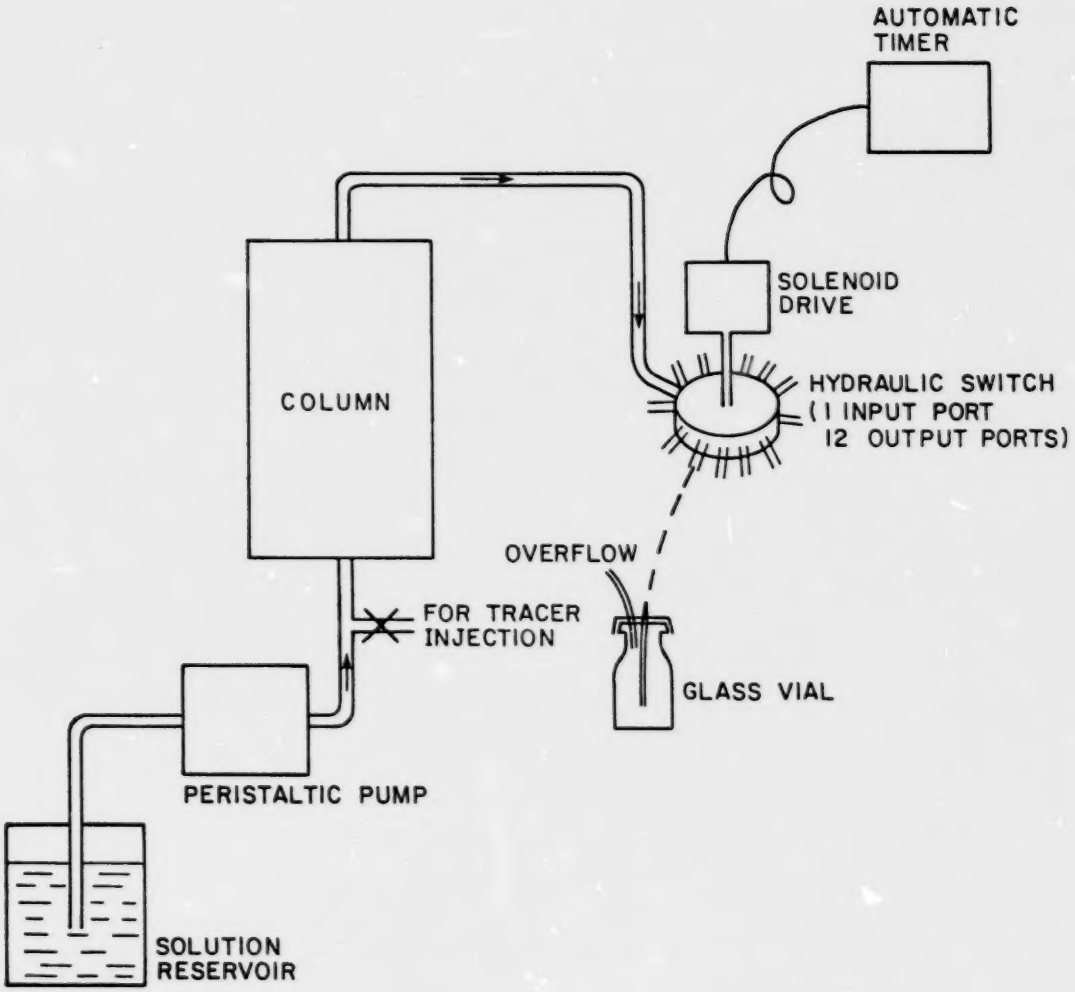


Figure 3: Schematic of the laboratory column apparatus.



The effluent was sampled at precise time intervals with an automated switching valve (Scanivalve) which was connected to twelve sampling ports. Each port was constructed of a feed line that connected to a sampling head which in turn was clamped to a 10 mL hypovial. A small Viton o-ring was used to maintain a tight seal between the sampling head and the hypovial. Column effluent was fed into the automated switching valve and, in turn, into the sample vials. Displaced air and excess sample volume were allowed to escape through an overflow line which was attached to the sampling head. As each hypovial was filled, a known volume of effluent (5-10 mL) was allowed to overflow into the overflow line and collection vial to provide an additional barrier between the sample and the atmosphere. As the last sample in a round was collected, the sampling head at each port was removed, and the sample was quickly sealed with a teflon-lined septum.

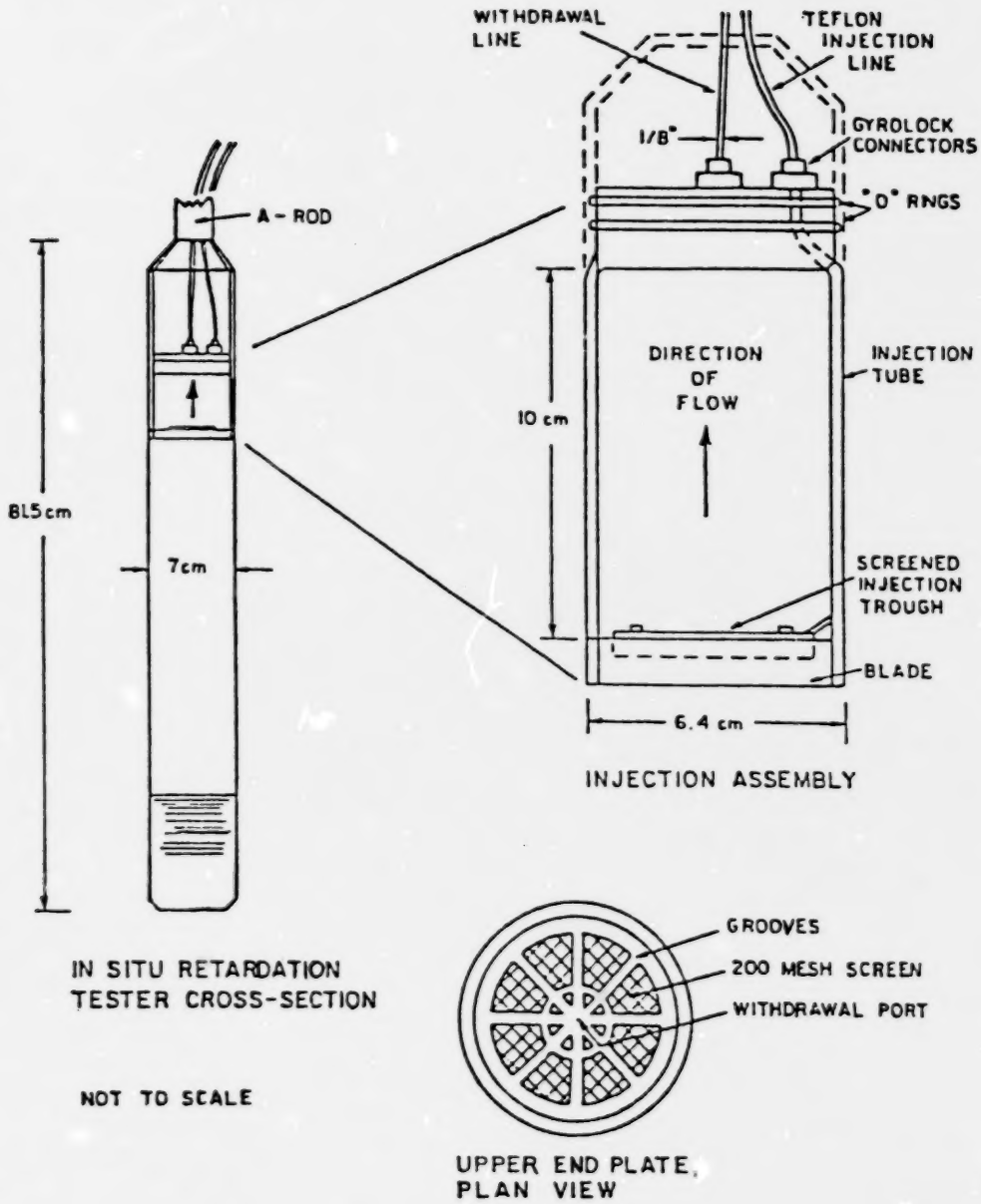
The column experiments were conducted using non-labelled compounds including benzene, toluene, and o-, m-, p-xylene. Only two of the eight geologic materials were tested, Borden sand and Rodney sand.

2.5 In Situ Column Experiments

The in situ column device was constructed of a stainless steel split-spoon sampler fitted with a screened end-plate, injection and sampling lines, and a screened injection port mounted along a knife edge. A diagram of the device is shown in Figure 4 and is a modification of the device described by Goodwin and Gillham (1982). The device was attached to drill rods, lowered into a hole augered to the water table and then driving until it was filled to the screened end-plate with sediment. The tester was completely sealed except for the opening at the bottom, through which groundwater could flow vertically.

To conduct the experiments, groundwater was pumped through the column of sediment with a peristaltic pump attached to the sampling line. When a stable flow rate and specific conductance were obtained, a 10 mL volume of groundwater spiked with a small amount

Figure 4: Schematic of the field column device



of Cl^- as a conservative tracer was introduced through the injection line to the screened port along the knife edge and thus into the moving groundwater. A flow-through conductance cell connected to a chart recorder was used to monitor the arrival of the conservative tracer in the outflow from the column. This information was used to determine if the device had been properly installed and for determinations of effective porosity.

For the reactive tracer breakthrough experiments, 10 mL of groundwater spiked with the test compounds was injected into the flow field in the same manner. As in the laboratory column experiments, the concentrations of each of the organic solutes in the injected solution was approximately 10 mg/kg (ppm). The materials used in the tester were stainless steel and Teflon, excluding a short length of flexible Viton tubing that passed through the peristaltic pump. Sampling of the effluent from the tester was accomplished in the same manner as in the laboratory pulse experiments. The samples were analyzed by gas chromatography as described below.

The in situ column method was used at two locations, the site of the natural-gradient tracer test at Borden, and at the location where the sample was collected at Rodney.

2.6 Analytical Methods

The organic compounds in samples for analysis by gas chromatography were first concentrated by a solvent extraction procedure. Hexane (1.0 mL) was added to a 10 mL sample vial. The sample was shaken for 15 minutes then allowed to sit for 10 to 30 minutes to allow the phases to separate. Approximately 2.5 μL of the hexane was then removed for injection into the gas chromatograph. The procedure is a modification of that given in Mackay et al. (1985) and Glaze et al. (1983) and is described in detail in Patrick et al. (1985). The samples were analyzed using a Shimadzu GC-9A gas chromatograph equipped with an FID detector and electronic integrator. The detection limit for the compounds used in this study was about 1 $\mu g/L$.

For samples containing labelled compounds, the activity of carbon-14 was determined on a Chicago-Nuclear Mark I Liquid Scintillation Counter with Beckman Ready-Solv Multi-purpose scintillation cocktail. Counting data were corrected for background, quenching, and dilution factors. The precision of the method was generally better than ± 3% and the detection limit was approximately 50 ng/L for each of the organic compounds.

The non-reactive tracers used in the column tests included tritium, chloride and specific conductance, depending upon the particular test. Tritium was analyzed using the MARK I Liquid Scintillation Counter, while chloride was determined using a Technicon Autonanalyzer II. Specific conductance, used in one field column test was measured using a flow-through conductivity probe and a YSI conductivity metre.

3

RESULTS AND DISCUSSION

3.1 Static Tests

Laboratory batch tests are conducted such that equilibrium (or near-equilibrium) is reached in the concentration between the solution and solid phases, prior to analysis. Consequently, this type of test is frequently referred to as a "static" test. Similarly, the correlation equations, eq. 5 and 6, were developed from the results of batch tests, so this too might be considered as a "static" method for evaluating K_d.

Figures 5a through 5h show the results of the batch tests plotted as the concentration of the solute in the solid phase versus the concentration in the solution phase at equilibrium. These graphs are referred to as sorption isotherms. Each figure includes the isotherms for all four compounds for a particular soil. Each data point of Figure 5 is the mean of three replicates and the solid lines are best-fit regression lines.

Visual inspection indicates the isotherms to be highly linear. This observation is supported by the high correlation coefficients (R) which in most cases are greater than 0.99 and never fall below 0.91. This provides strong evidence that for the soils and organic compounds used, sorption is indeed a linear process and therefore the K_d model for representing the effects of geochemical reactions on the transport process should be appropriate. Karickhoff (1984) suggests that if the equilibrium aqueous phase concentration of a hydrophobic solute is less than one half of its aqueous solubility and below 10^{-5} M, it can be expected that sorption isotherms measured in natural systems will be linear. The range in concentration covered in the batch experiments of this study were all well below one half of the compounds solubility and less than or approximately equal to 10^{-5} M. Thus, the linearity observed is consistent with the theoretical considerations of Karickhoff (1984).

Table 3: Results of K_d determinations using correlation equations based on f_{oc} and as determined from the batch tests.

SOIL	F.O.C.	Kd (mL/g)			
		BENZENE	TOLUENE	P-XYLENE	NAPHTHALENE
NORTH BAY	0.00017				
Kd-S		0.052	0.099	0.200	0.487
-Kow		0.018	0.038	0.097	0.151
-Batch		0.031	0.057	0.119	0.120
WOOLWICH	0.00023				
Kd-S		0.070	0.133	0.270	0.659
-Kow		0.025	0.051	0.132	0.204
-Batch		0.079	0.157	0.383	0.648
CHALK RIVER	0.00026				
Kd-S		0.080	0.151	0.306	0.745
-Kow		0.028	0.058	0.149	0.231
-Batch		0.051	0.072	0.190	0.280
BORDEN	0.00028				
Kd-S		0.086	0.162	0.329	0.802
-Kow		0.030	0.062	0.160	0.248
-Batch		0.070	0.123	0.261	0.353
OTTAWA	0.00060				
Kd-S		0.184	0.348	0.706	1.719
-Kow		0.065	0.134	0.343	0.532
-Batch		0.885	4.152	7.536	9.033
CAMBRIDGE	0.00065				
Kd-S		0.200	0.377	0.764	1.862
-Kow		0.070	0.145	0.372	0.577
-Batch		0.150	0.289	0.805	2.011
RODNEY	0.00102				
Kd-S		0.312	0.592	1.200	2.922
-Kow		0.110	0.227	0.583	0.905
-Batch		1.800	8.296	11.976	21.800
WILDWOOD	0.00108				
Kd-S		0.330	0.626	1.270	3.094
-Kow		0.117	0.241	0.618	0.958
-Batch		0.092	0.199	0.569	1.573

Values of K_d were determined as the slope of the regression lines fitted to the sorption data. These are given in Table 3, along with the f_{oc} of the aquifer materi , and the K_d values calculated using eq. 5 and the correlation equations, 6 and 7.

Comparing Tables 1 and 3, it can be seen that the data is entirely consistent with the solubility and K_{ow} values of the compounds. That is, for all soils, the batch K_d values increase with increasing K_{ow} or decreasing solubility. Thus, as shown by others, the hydrophobicity of the compound has a significant effect on its sorptive properties. The K_d values determined from the correlation equations show the same trend; however, this is a necessary consequence of the form of the equations.

The aquifer materials in Table 3 are listed in order of increasing f_{oc}. Looking down the table, as expected, and as the correlation equations predict, the batch K_d values tend to increase with increasing f_{oc}; there are however, several notable exceptions. The Woolwich soil has K_d values that are approximately two to three times greater than the Chalk River soil, even though the reported f_{oc} value is slightly less. This is not taken to be a major discrepancy however, and may simply reflect the uncertainty in the measured f_{oc} values. The Ottawa and Rodney soils appear to be substantial exceptions to the trend. While the batch K_d values for the other soils are generally within a factor of two of those predicted by the correlation equations, the batch values for the Ottawa and Rodney soils exceed those of the correlation equations in most cases by more than an order of magnitude. Based on the results of the column tests, as presented in the following section, the inconsistency appears to be in the results of the batch tests. Both the f_{oc} measurements and batch tests were repeated however the results remained essentially the same. At this point there is no apparent explanation for the inconsistent behaviour of the Rodney and Ottawa samples.

Neglecting the Ottawa and Rodney soils, and considering the difficulty in measuring very low f_{oc} values, the K_d values determined from the correlation equations are reasonably

close to the batch values. Nevertheless, consistent differences are evident. Values determined on the basis of solubility are generally greater than the batch values, but usually a factor of no more than two, and for three of the soils, Woolwich, Borden and Cambridge, the solubility correlation and batch values are very close. Correlations based on K_{ow} are generally less than the batch values by a factor of two. The results suggest that the correlation procedure based on solubility gives a better prediction than the procedure based on K_{ow}. It may be possible however to obtain improved predictions for both models using different values of the parameters (A, B, C and D of equations 6 and 7).

Figure 5a. Sorption isotherms for North Bay sand.

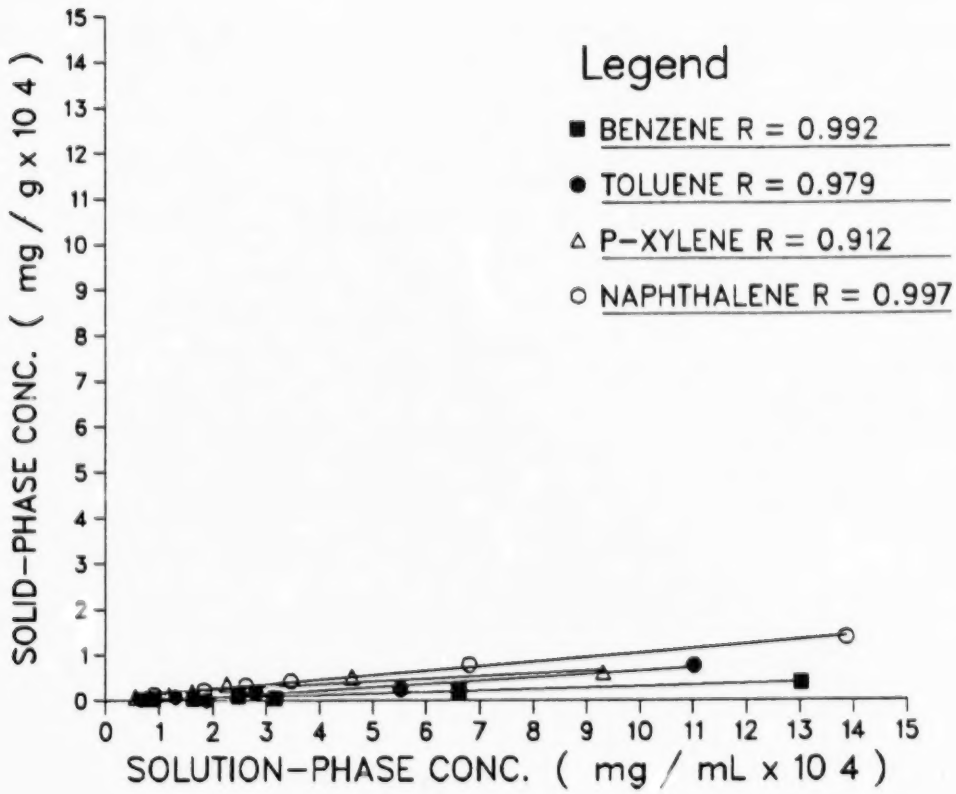

Legend
BENZENE R = 0.992
TOLUENE R = 0.979
P-XYLENE R = 0.912
NAPHTHALENE R = 0.997
SOLID-PHASE CONC. (mg / g x 10 4)
SOLUTION-PHASE CONC. (mg / mL x 10 4)
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

Figure 5 b. Sorption isotherms for Woolwich sand.

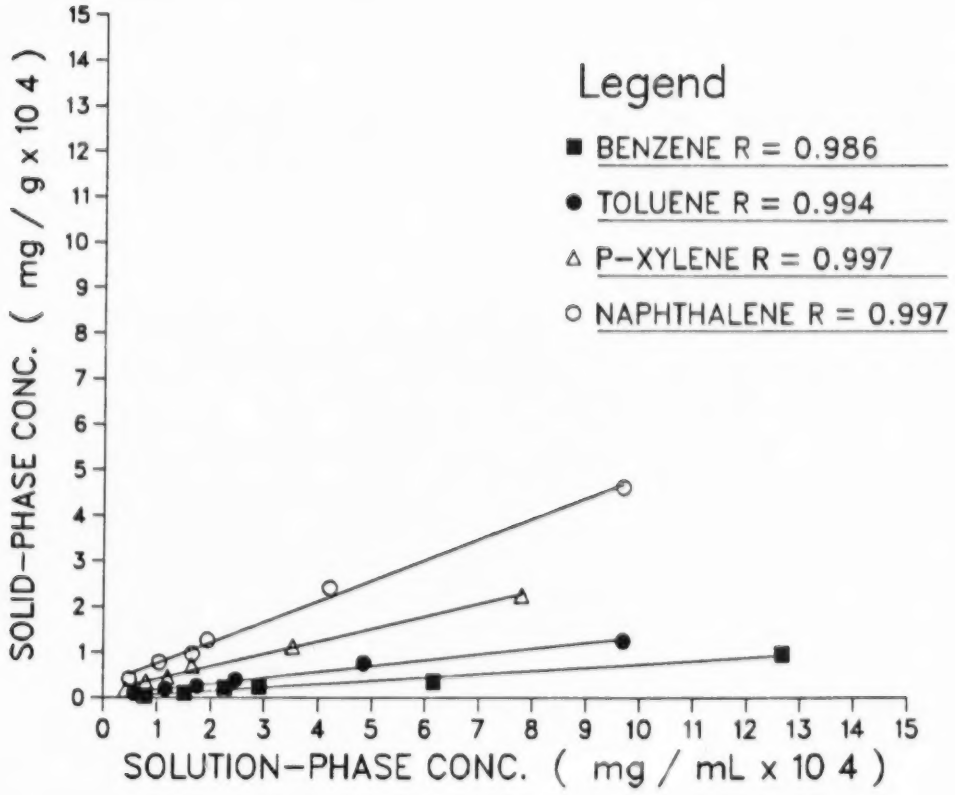

Legend
BENZENE R = 0.986
TOLUENE R = 0.994
P-XYLENE R = 0.997
NAPHTHALENE R = 0.997
SOLID-PHASE CONC. (mg / g x 10 4)
SOLUTION-PHASE CONC. (mg / mL x 10 4)
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

Figure 5c. Sorption isotherms for Chalk River sand.

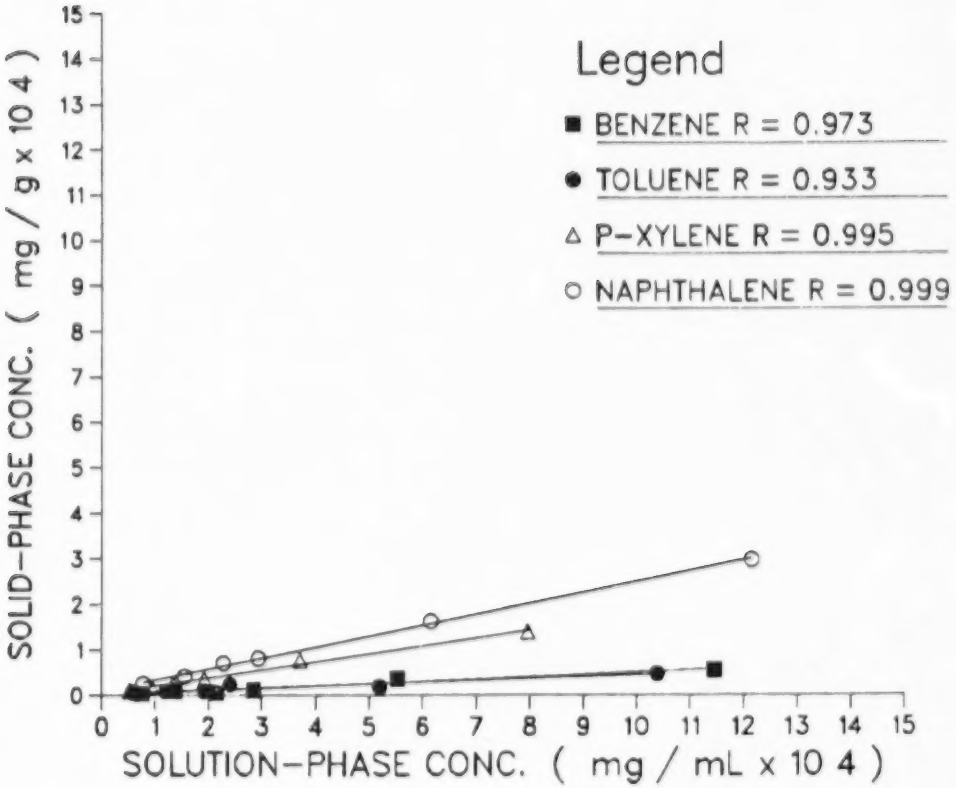

Legend
BENZENE R = 0.973
TOLUENE R = 0.933
P-XYLENE R = 0.995
NAPHTHALENE R = 0.999
SOLID-PHASE CONC. (mg / g x 10 4)
SOLUTION-PHASE CONC. (mg / mL x 10 4)
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

Figure 5d. Sorption isotherms for Borden sand.

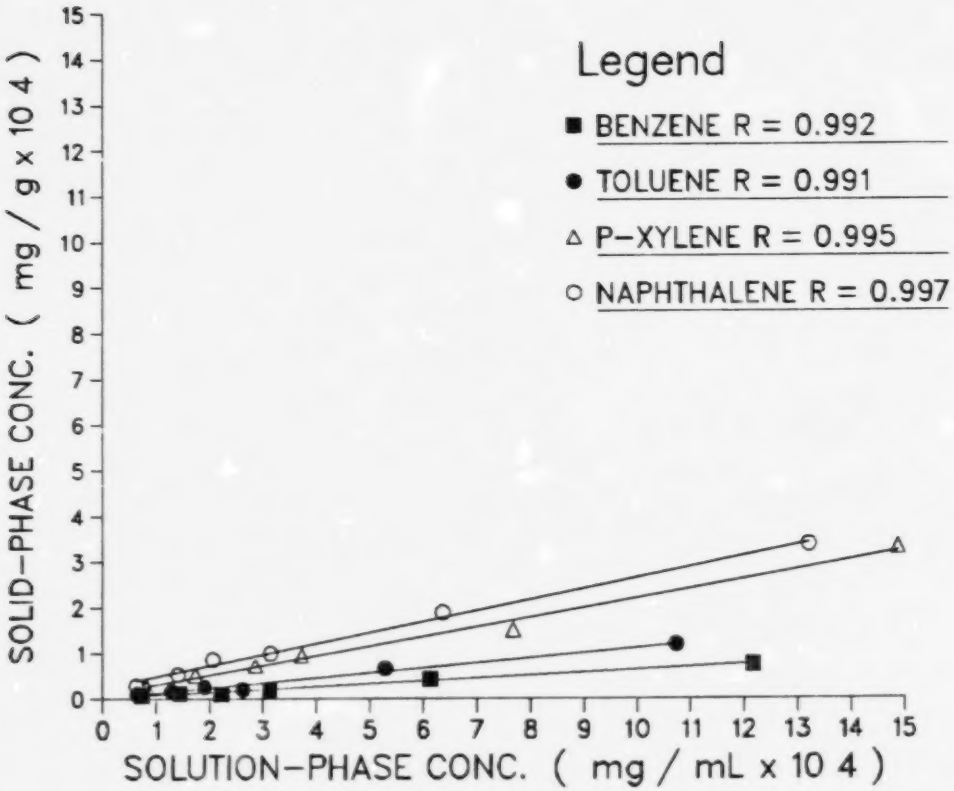

Legend
BENZENE R = 0.992
TOLUENE R = 0.991
P-XYLENE R = 0.995
NAPHTHALENE R = 0.997
SOLID-PHASE CONC. (mg / g x 10 4)
SOLUTION-PHASE CONC. (mg / mL x 10 4)
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

Figure 5e. Sorption isotherms for Ottawa sand.

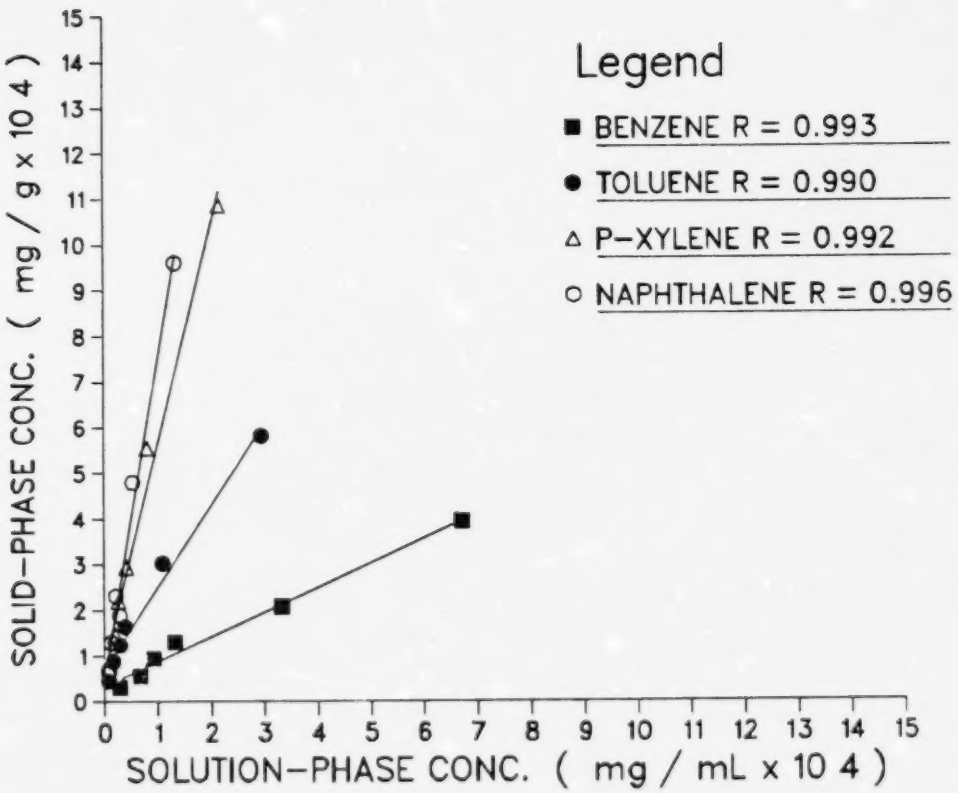

SOLID-PHASE CONC. (mg / g x 10 4)
SOLUTION-PHASE CONC. (mg / mL x 10 4)
Legend
BENZENE R = 0.993
TOLUENE R = 0.990
P-XYLENE R = 0.992
NAPHTHALENE R = 0.996

Figure 5f. Sorption isotherms for Cambridge sand.

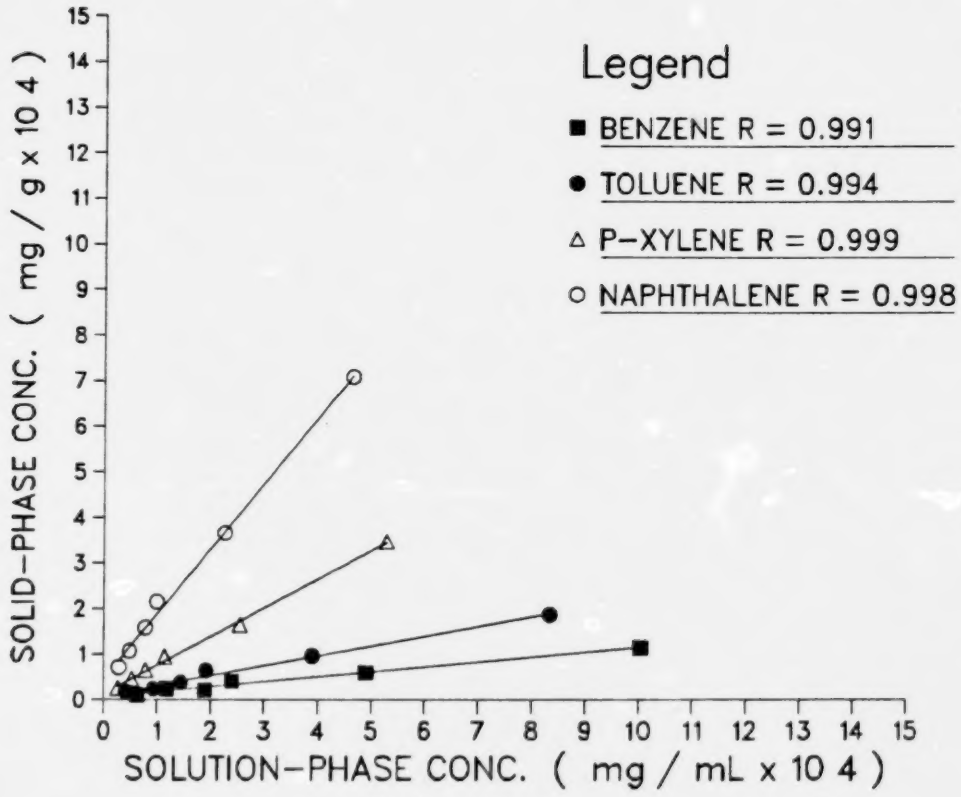


Figure 5g. Sorption isotherms for Rodney sand.

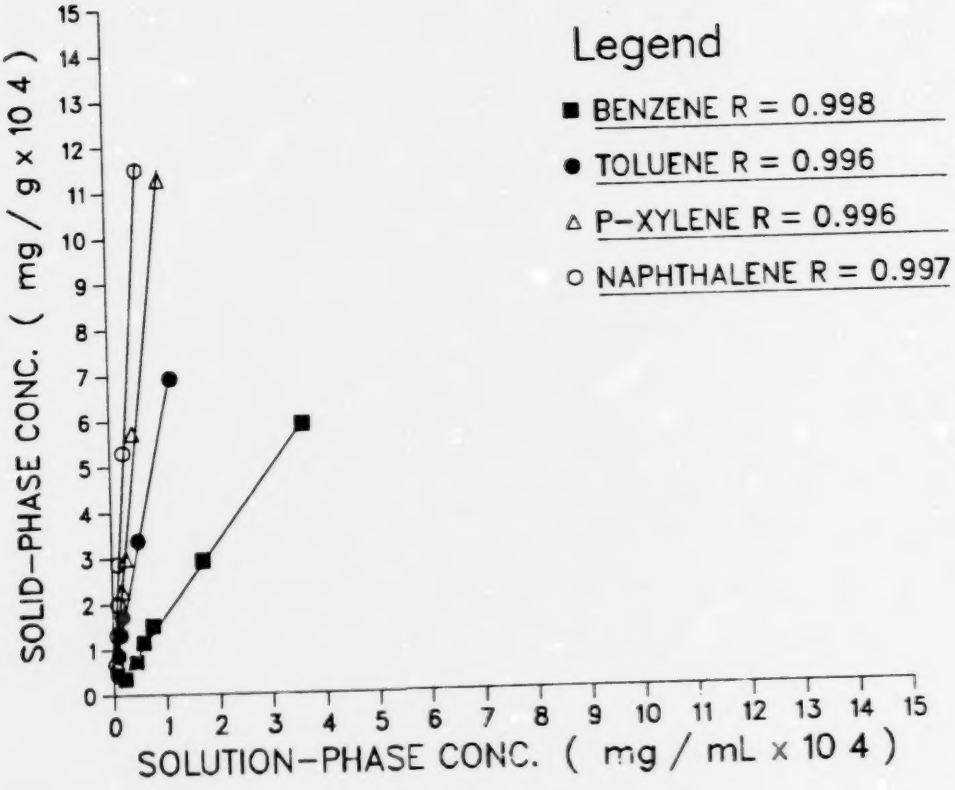
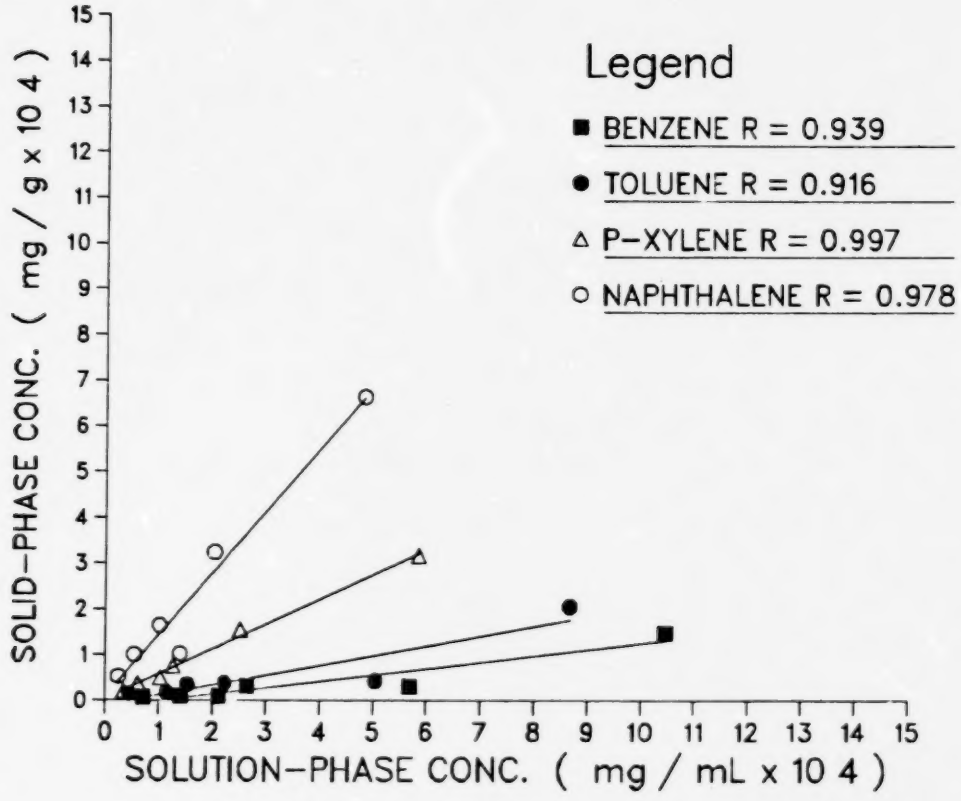


Figure 5h. Sorption isotherms for Wildwood sand.



3.2 Dynamic Tests

In the column tests, both laboratory and field, the retardation factor is determined from the time of arrival of the reactive species with respect to that of a non-reactive species. The K_d values can then be calculated using [4], provided the bulk density and porosity of the porous medium are known. Because the K_d values are determined while the water (and solutes) are moving through the medium, column tests are frequently referred to as dynamic tests. It can be argued that the results of dynamic tests should be more representative of the dynamic conditions that exist in the field, than static tests.

Results obtained from the laboratory column studies for Borden sand are given in Figures 6 and 7. In these diagrams the normalized effluent concentration, C/C_o, is plotted against dimensionless time (Pore Volumes). C is the concentration measured in the effluent, C_o is the influent concentration and the number of pore volumes is the volume of effluent divided by the total volume of voids in the column. For each breakthrough curve the values of C/C_o versus dimensionless time were connected with straight lines.

A progressive departure from one pore volume of the arrival time of the organic solutes was observed, indicating a progressive increase in the degree of retardation, with benzene showing the least retardation and p-xylene the greatest. The measured concentration profiles were observed to be highly asymmetrical relative to the concentration profiles measured for the conservative tracers. Although this asymmetry and tailing is inconsistent with the behaviour of the conservative tracer (not shown), it is a common characteristic of reactive solutes, with similar behaviour having been reported by Kay and Elrick (1967), Lindstrom and Boermsa (1971), van Genuchten et al. (1977), and others. This behaviour has been attributed to apparent nonequilibrium conditions in the porous medium (Kay and Elrick, 1967 and van Genuchten et al., 1977) and to spatial differences in sorption characteristics due to soil-pore geometry and distribution (Lindstrom and Boermsa, 1971).

Figure 6: Laboratory column results for Borden sand. v = 22 cm/day.

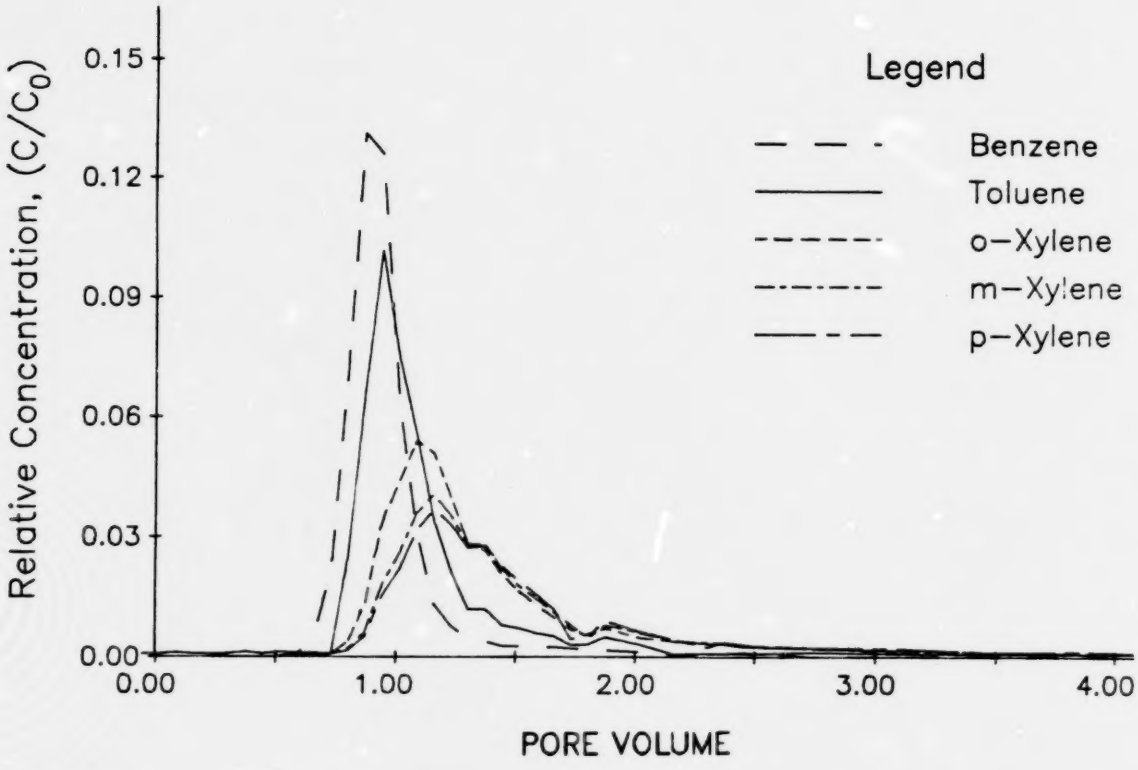
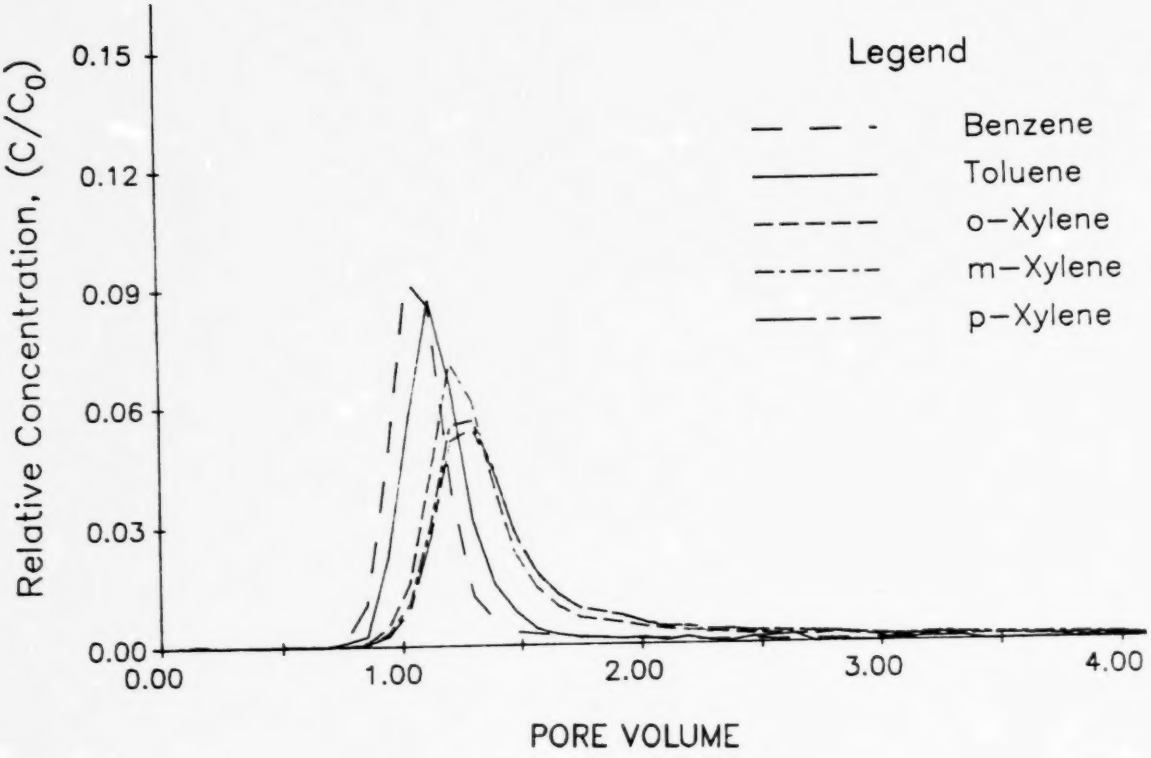


Figure 7: Laboratory column results for Borden sand, v = 150 cm/day.



Values of the mean arrival time were calculated for each of the tracers in each of the experiments by determining the position of the centre of mass of the respective breakthrough curves. Retardation factors were then calculated by dividing the mean arrival time of the organic solute by the mean arrival time of the non-reactive tracer.

Results of the field column experiments are given in Figure 8 and 9. The data is presented as normalized effluent concentration versus dimensionless time as defined for the laboratory column results.

The transport of the organic solutes observed in the field experiments was consistent with the laboratory results. All five compounds were retarded with respect to the conservative tracer and the order of retardation was the same as observed in the laboratory experiments. At the lower velocity of 190 cm/day, the retardation was somewhat greater than for the higher velocity.

The retardation values were determined from the field breakthrough curves using the same one-dimensional approach that was used to analyze the results of the laboratory column experiments. Because the solutes were injected as a line source in the field experiments, the assumption of one-dimensional transport may not be satisfied. Although this could lead to errors in the calculated R values, because R is determined by comparing the effluent history of the reactive solute with the non-reactive solute, the error is expected to be very small.

The bulk density and porosity of the laboratory column was 1.7 g/cm^3 and 0.34 respectively. Measurements could not be made on the field column and thus the same values were assumed to apply. Using these values and [4], the measured retardation factors were converted to K_d.

The K_d values determined by all methods for Borden sand are included in Table 4. Also given are the values calculated from the retardation factors obtained from the natural gradient tracer test reported by Patrick et al. (1986).

Figure 8: Field column results for Borden sand. v = 340 cm/day.

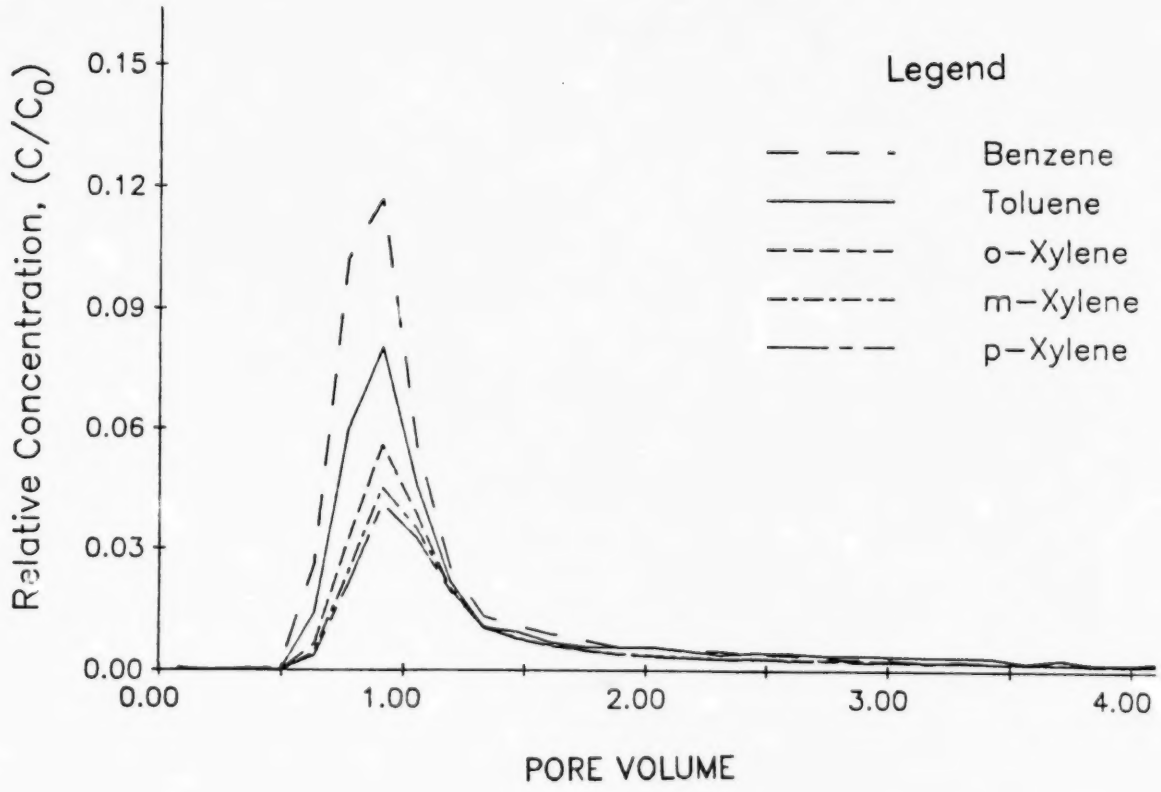


Figure 9: Field column results for Borden sand. v = 190 cm/day.

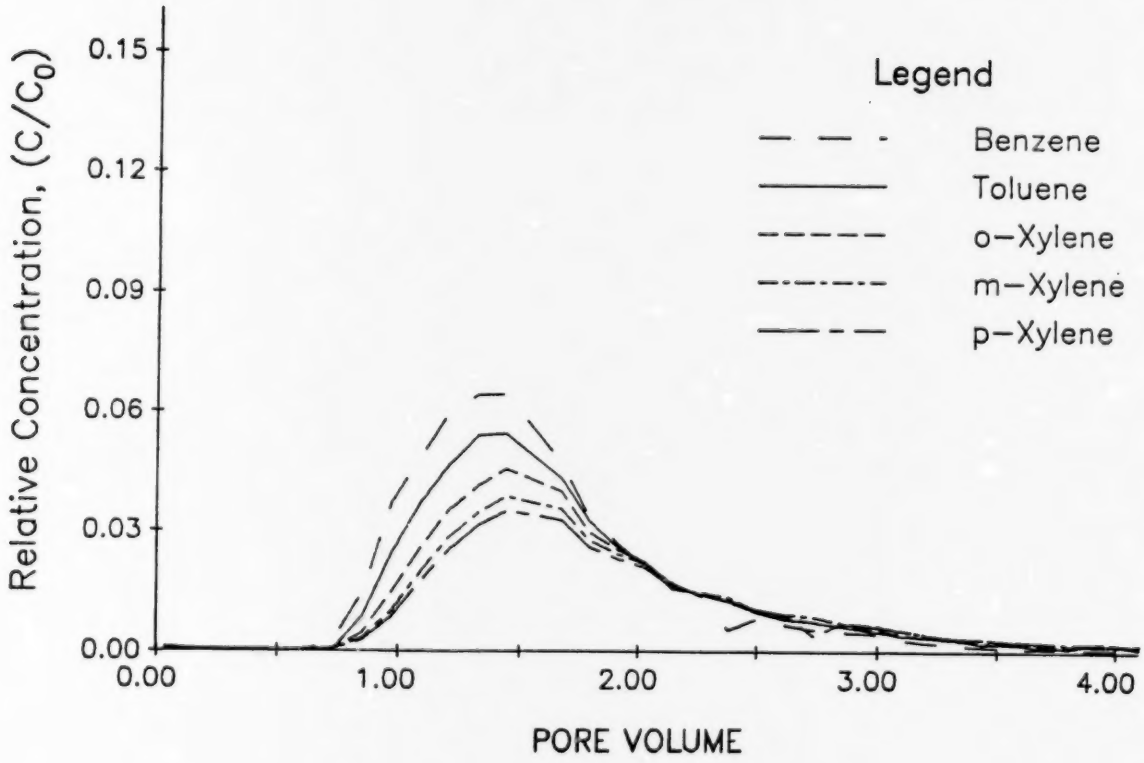


Table 4: Comparison of distribution coefficients for Borden sand.

CHEMICAL	CALCULATED		BATCH	COLUMN				FIELD TRACER TEST*
	S	Kow		In situ V(cm/day)		Laboratory V(cm/day)		
				340	190	150	22	
BENZENE	0.09	0.03	0.07	0.06	0.08	0.02	0.00	0.02
TOLUENE	0.16	0.06	0.12	0.06	0.10	0.04	0.04	0.04
O-XYLENE	0.32	0.11	--	0.06	0.14	0.06	0.06	0.09
M-XYLENE	0.36	0.17	--	0.08	0.16	0.08	0.08	0.13
P-XYLENE	0.33	0.16	0.26	0.08	0.16	0.08	0.10	0.09
NAPHTHALENE	0.80	0.25	0.35	--	--	--	--	--

* From Patrick et al., 1986.

The laboratory column results for the Rodney sample, including breakthrough curves for the non-reactive tracer and for the organic compounds measured at three different velocities, are given in Figures 10 through 13. The high K_d values indicated by the batch test results indicated that very long times would be required to complete a column experiment. To avoid this difficulty the column length was reduced from 10 to 5 cm. In addition, the results obtained from the Borden column tests indicated a substantial loss in mass, particularly for toluene and the three isomers of xylene. Subsequent tests suggested that some of the apparent loss in mass could be caused by biodegradation. Thus for the Rodney laboratory column tests, sodium azide was added to the influent solution (1.0% by weight).

Based on the high batch K_d values, it was not considered practical to conduct the field column tests for the highly sorbed compounds because of the long duration of the tests. Consequently only benzene and toluene were included in the tracer solution. The results of the field column tests are given in Figure 14 and the K_d values determined by all methods are included in Table 5.

The results of all the column experiments using the organic solutes have two very distinctive features. They are all asymmetrical as discussed previously, and they all indicate a significant loss in mass.

Mass balance calculations indicated that generally about 80% of the benzene that was injected was recovered in the samples. The percent recovery declined however, with as little as 40% of the p-xylene being recovered in some cases. Because of the methods of tracer injection and sample collection, it is difficult to perform accurate mass balance calculations on the column data. Nevertheless, because the data is plotted as relative concentration, for any given experiment, the area under the curve should be the same for all compounds. This clearly is not the case, with the area decreasing (greater mass loss) with increasing hydrophobicity of the compound. The addition of azide to the influent solution used in the Rodney soil did not substantially improve the apparent lack of mass recovery.

Figure 10: Breakthrough curve for the non-reactive tracer (tritium) in Rodney sand (v = 224 cm/day).

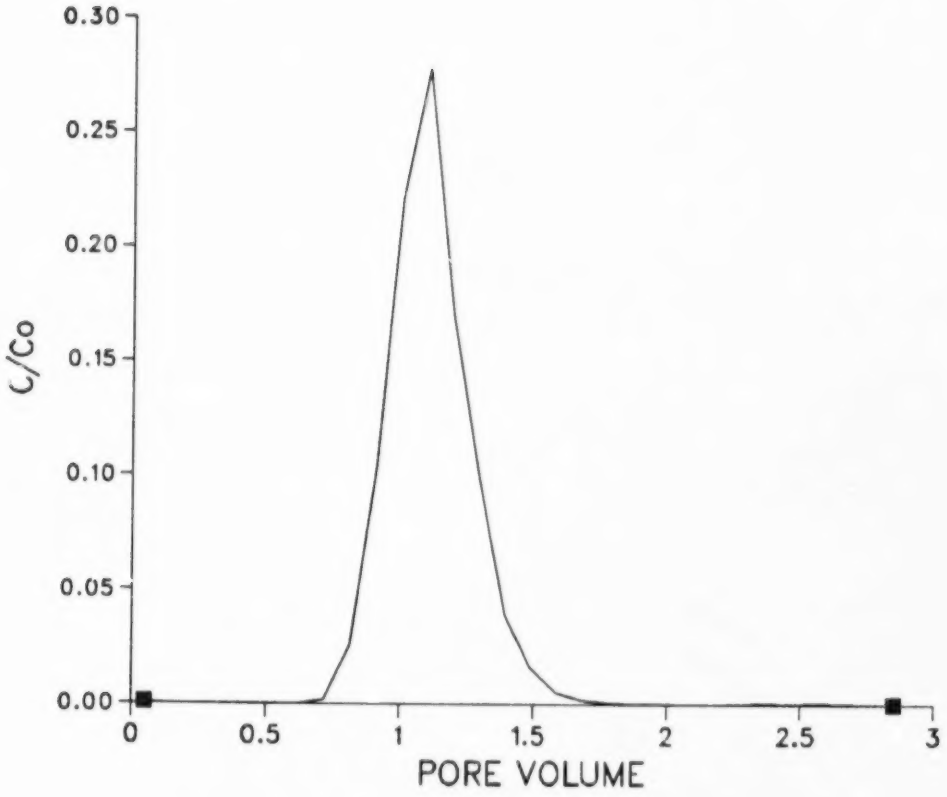


Figure 11: Laboratory column result from Rodney sand. v = 37 cm/day.

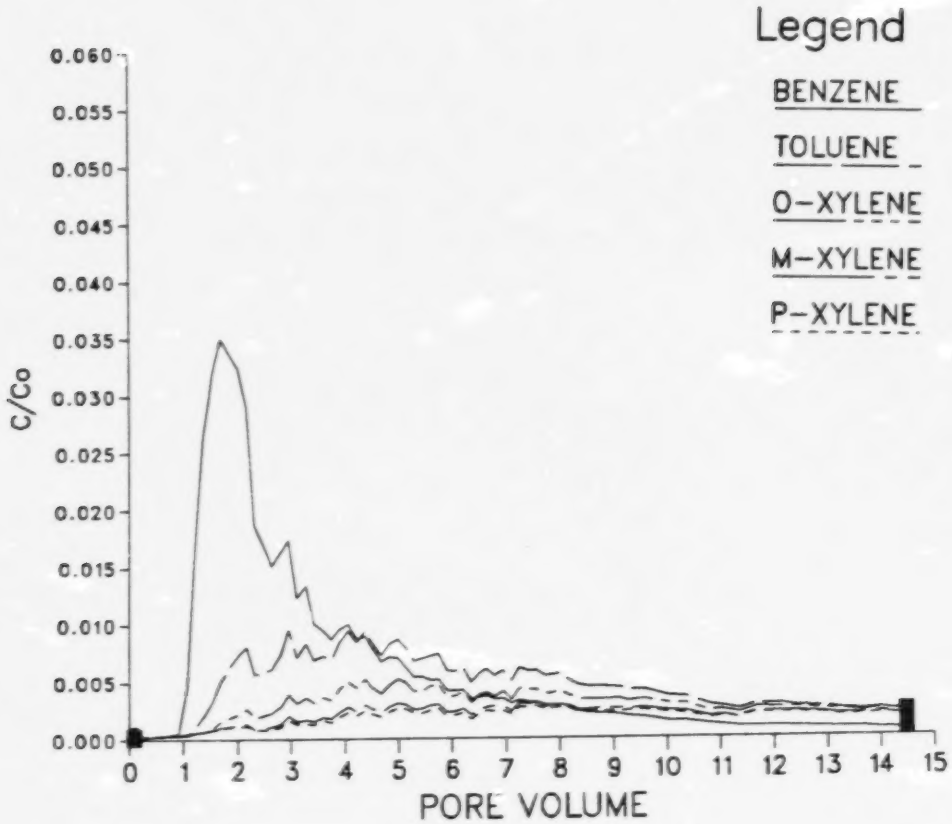


Figure 12: Laboratory column result for Rodney sand, v = 75 cm/day.

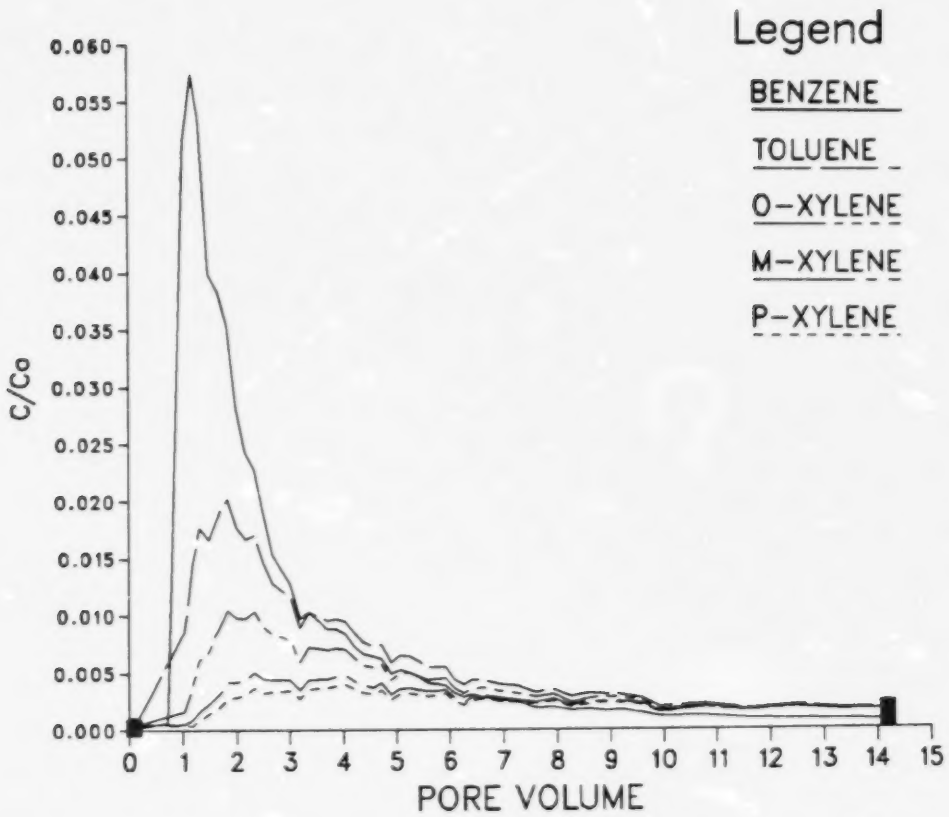


Figure 13: Laboratory column result for Rodney sand. v = 224 cm/day.

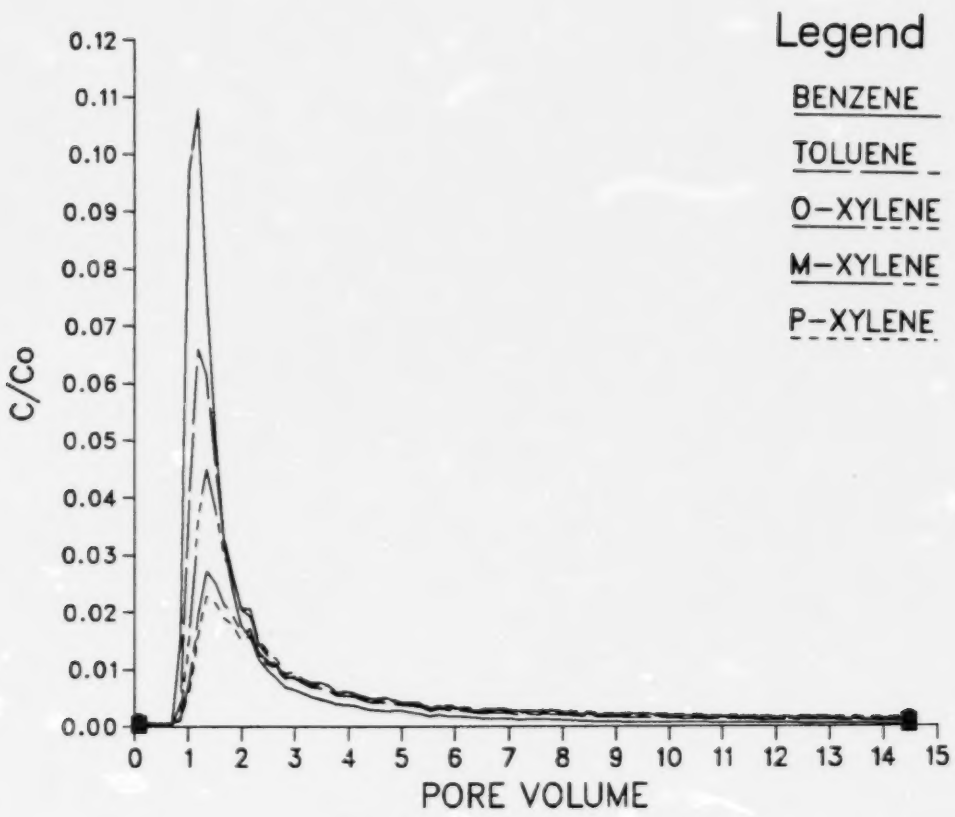


Figure 14: Result of field column test for Rodney sand, v = 465 cm/day.

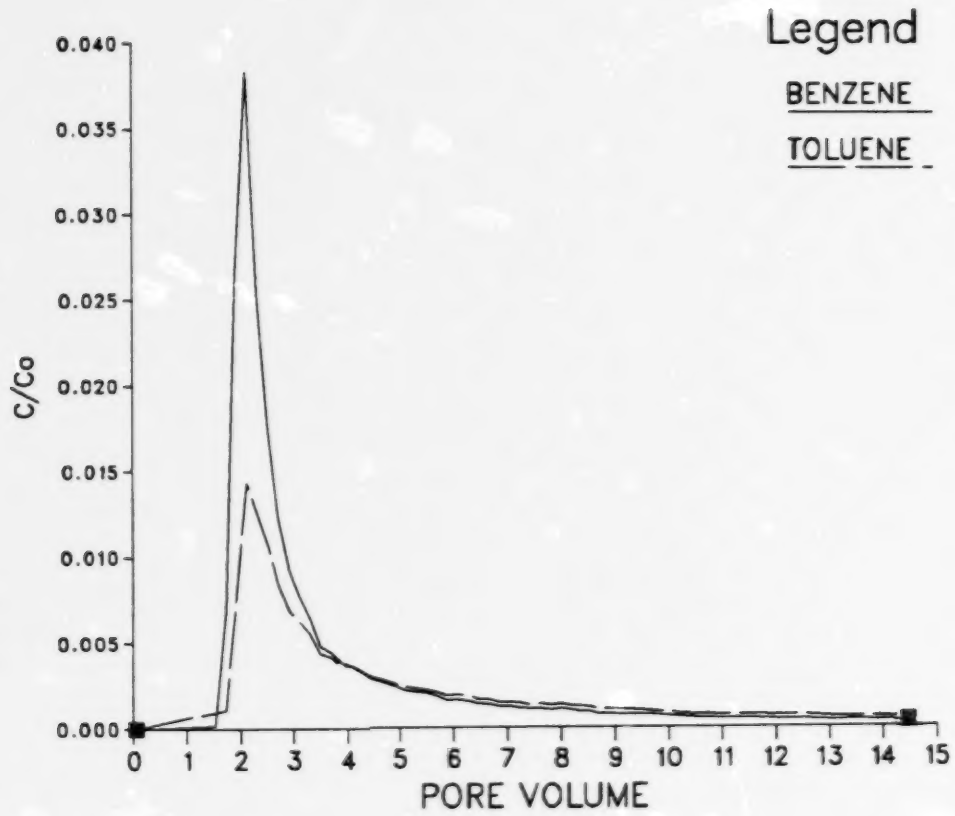


Table 5: Comparison of distribution coefficient for Rodney sand.

CHEMICAL	CALCULATED		BATCH	COLUMN			
				In situ	Laboratory		
	S	Kow		V(cm/day)	V(cm/day)		
				465	224	75	37
BENZENE	0.31	0.11	1.80	0.50	0.21	0.38	0.53
TOLUENE	0.59	0.23	8.30	0.73	0.36	0.73	1.08
O-XYLENE	1.16	0.42	--	--	0.46	0.92	1.36
M-XYLENE	1.31	0.63	--	--	0.57	1.24	1.55
P-XYLENE	1.20	0.58	11.98	--	0.62	1.37	1.61
NAPHTHALENE	2.92	0.91	21.80	--	--	--	--

This suggests that the loss is not caused by biodegradation. The remaining possibilities include volatilization during sample collection or some irreversible sorption process. Though we believe that volatilization is a significant factor, the possibility of irreversible sorption can not be dismissed.

Referring to Table 4 for the Borden soil, all methods gave K_d values that increased with increasing hydrophobicity of the compound. Furthermore, all methods, including both types of column tests and the field tracer tests gave results that were very similar. It should be noted that there is no apparent trend in K_d with velocity in the column experiments, and thus no indication that retardation is affected by the kinetics of the sorption process.

Considering the uncertainties that are inherent in the respective methods, it would be reasonable to consider the results to be identical. However, the apparent similarity may be the result of the very low K_d values for the Borden sand. Greater differences between methods might be expected in the Rodney soil, which has a higher f_{oc} value.

Referring to Table 5, with the exception of the batch results, the K_d values are quite similar. Considering the laboratory column results, there is a distinct trend with velocity, with the K_d values decreasing with increasing velocity. This suggests that the retardation process is indeed affected by kinetic exchange processes. It appears that at higher velocities equilibrium is not reached, leading to an apparent K_d that is lower than determined at low velocities. Indeed, the apparent K_d varies by about a factor of two over the velocity range that was used in the study. The K_d values determined at the lowest velocity are greater than, but close to, the values determined using the correlation equation based on solubility. The correlation based on K_{ow} gave K_d values that are substantially lower. The two values determined in the in situ column test (benzene and toluene) are similar to the values calculated on the basis of solubility and the low-velocity laboratory column test. It should be noted however, that the field column test was conducted at a velocity that was more than

ten times greater than the slowest laboratory column. This appears to contradict the velocity dependence indicated by the laboratory test. The apparent inconsistency could be the result of the method or could simply be the result of geologic heterogeneity. Though the tester was installed near the site from which the soil sample was collected, it may have been located in a zone having a slightly higher f_{oc}.

Because the actual K_d values are unknown, there is no basis for suggesting that one method is more accurate than another. The results do suggest however, that if column procedures are used, they should be conducted at a velocity similar to the groundwater velocity at the site of interest.

3.3 Comparison of Methods

Because there is no absolute against which the test results can be compared, there is no basis for suggesting a particular method to be the most accurate. However, as a guide to selecting a method, Table 6 compares the advantages and disadvantages of the methods used in this study.

Table 6: Summary of advantages and disadvantages of the small-scale K_d tests used in this study

METHOD	ADVANTAGES	DISADVANTAGES
Correlation Equations	- only analytical requirement is f_{oc} - relatively simply - inexpensive - minimal equipment requirements - give results that are internally consistent and reasonably consistent with other methods	- theoretically based but essentially empirical - no assurance equation applicable to a particular soil. - do not account for sorption in mineral phase. may be important in fine-grained materials - different equations and different parameter values are available; the best choice not always clear. - accurate measurements of f_{oc} difficult in low-carbon materials f_{oc} soils.
Batch	- provide a direct measure for the particular soil and organic compound - applicability of K_d can be assessed on basis of isotherm linearity - can be used to evaluate effects of factors such as changing competition for sorption sites.	- because of volatility and sorption onto many labware materials, the tests require specialized equipment and skilled and experienced staff - relatively expensive analytical equipment - K_d values applicable to static conditions
Lab Column	- provides K_d value appropriate for dynamic cnditions - because K_d values are calculated from relative times of arrival, small losses due to volatilization should not affect the results - can examine velocity sensitivity of K_d	- specialized and expensive equipment. - time consuming and thus costly. - apparent mass loss and asymmetry remain as technical uncertainties - inconvenient for soils with low hydraulic conductivity and very high K_d values
Field Column -	The field column has advantages and disadvantages similar to the laboratory column. In addition, it insures that the measurement is made under natural geochemical conditions. On the other hand, being performed in the field, the tests are more costly and the least convenient of those considered.	

4

CONCLUSIONS

The aquifer materials selected for use in this study covered a wide range in f_{oc} (0.00017 to 0.00108). Corresponding to this range, the K_d values for the most weakly sorbed compound, benzene, varied from about 0.03 to 0.09 mL/g, while values for the most strongly sorbed compound, naphthalene, varied from about 0.15 to 2.0 mL/g. Assuming values of 1.7 g/cm^3 and 0.34 for bulk density and porosity respectively, benzene could be expected to have retardation values between 1.1 and 1.4 in aquifer materials typical of southern Ontario. Similarly, retardation values for naphthalene could vary between 1.7 and 10. The other compounds used in this study lie between these extremes. It is apparent that retardation factors for constituents of petroleum products can range from values where the velocity of the contaminant will be almost that of the groundwater (1.1), to value where the velocity of the contaminant is substantially less than that of the groundwater (10). An appreciation of the magnitude of the retardation factor can therefore be an important consideration in the assessment of environmental impact or in the design of remediation schemes. It follows that reliable methods for determining retardation factors or K_d values are required.

The trends in the K_d values of this study are consistent with the theory of sorption for hydrophobic organic compounds. The order of sorption for any particular soil showed increasing sorption with increasing hydrophobicity, and though exceptions were noted, the K_d of all the compounds increased with increasing f_{oc}. Of particular importance, the correlation method based on solubility gave values that were reasonably close to the measured values over the entire range of compounds and over the entire range of f_{oc} values. This is

noteworthy because the method is not generally recommended for materials having f_{oc} values less than 0.001; however most aquifers may have lower f_{oc} values. The result suggests that the correlation method may indeed be appropriate for determining K_d values in aquifers of low f_{oc}.

Suggesting the most appropriate method for evaluating K_d is a difficult task. Each method has technical advantages and disadvantages and to some extent, the most appropriate method would be determined by the particular application. Cost and analytical requirements are other factors that could affect the choice.

Considering cost, convenience and accuracy, the correlation methods appear to be the most appropriate for most practical applications. A key element in this procedure is that accurate f_{oc} values of the sediments of interest be determined. In making the measurements, known standards should be included with the samples, and of course a laboratory experienced in low f_{oc} measurements should be used. In this study the correlation equation based on solubility gave results that were closer to the batch test and column results than correlations based on K_{ow}. Though the method appears to give reasonable results, there may be room for improvement through further refinement of the parameter values.

Because of the empirical nature of the correlation equation and the short period of experience, it would probably be advisable to check the results with a small number of batch tests. In situations where very high groundwater velocities are expected, such as in very coarse grained aquifers or near pumping wells, it could be advisable to supplement the empirical predictions with a small number of dynamic tests (laboratory or field column). It should also be noted that the correlation procedures do not account for sorption onto the mineral phase. This does not appear to be a limitation in coarse grained materials typical of aquifers; however, the method is highly suspect in materials with a significant clay fraction.

5

GLOSSARY OF CONTAMINANT HYDROGEOLOGY TERMS

Advection. The process by which compounds are transported in groundwater by the bulk motion of the flowing groundwater.

Chemical Precipitation. The process whereby dissolved compounds or elements combine to form a solid phase, thus removing mass from solution.

Chemical Transformation. The process in which compounds especially contaminants, are chemically changed by non-biological processes, such as hydrolysis, oxidation, and reduction.

Conservative Solute. A dissolved compound which does not undergo retardation processes and so moves at the same velocity as the groundwater. Chloride ion is a common example. Also termed non-reactive solute.

Dispersion. The process by which dissolved compounds (solutes) spread out from the path that they would be expected to follow according to advection. Also called hydrodynamic dispersion.

Distribution Coefficient. (K_d) Ratio of the concentration of a solute in the solid phase to the concentration in the solution phase. Applicable under conditions of equilibrium partitioning.

Hydrophobicity. A measure of an organic compounds aversion to occurring as an aqueous solute.

Microbial Transformation. Also termed *biochemical degradation* and *biodegradation.* The process in which compounds, especially contaminants, are chemically changed where the process is carried out by micro-organisms.

Octanol-water partition coefficient. (K_{ow}) An experimental value which expresses the amount of a compound that occurs in an octanol phase relative to the amount that occurs in an aqueous (water) phase when the compound is allowed to partition itself between these coexisting phases.

Organic Carbon Content. (f_{oc}) Is the solid-phase organic carbon content of a soil, generally expressed as mass of carbon per unit mass of soil.

Organic Carbon Partitioning Coefficient. (K_{oc}) Is a measure of the partitioning of an organic solute between the water phase and the solid organic carbon phase of a soil material.

Retardation. The process by which dissolved compounds travel less quickly than does the bulk groundwater. Retardation results from processes such as sorption, chemical precipitation and biodegradation.

Solute. An element or compound that is dissolved in a solvent such as groundwater.

Sorption. The retardation process whereby some of the solute mass is held by the solid phase while the rest is held in solution. During advection, this process slows the compound causing retardation. In detail, the step where solute is transferred to the solid phase is *(ad)sorption* and the step where solute is transferred from the solid to solution is *desorption.*

6

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